

CHEMISTS MANUAL OF
NON-FERROUS ALLOYS

MODERN WORKS OF REFERENCE

Pocket-Book for Chemists, Chemical Manufacturers, Metallurgists, Dyers, Distillers, Brewers, Sugar Refiners, Photographers, Students, etc. By THOMAS BAYLEY, Assoc. R.C.Sc.I. Edited by ROBERT ENSOLL, F.C.S., Assistant Chemist to the British Dyes Ltd. Eighth Edition, with 196 Tables, xvi + 425 pp., fcap. 8vo. 10s. 6d. net. Postage, 5d.; abroad, 8d.

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CHEMISTS' MANUAL OF NON-FERROUS ALLOYS

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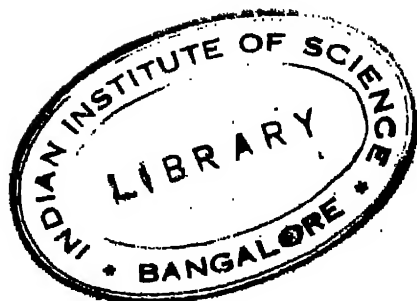
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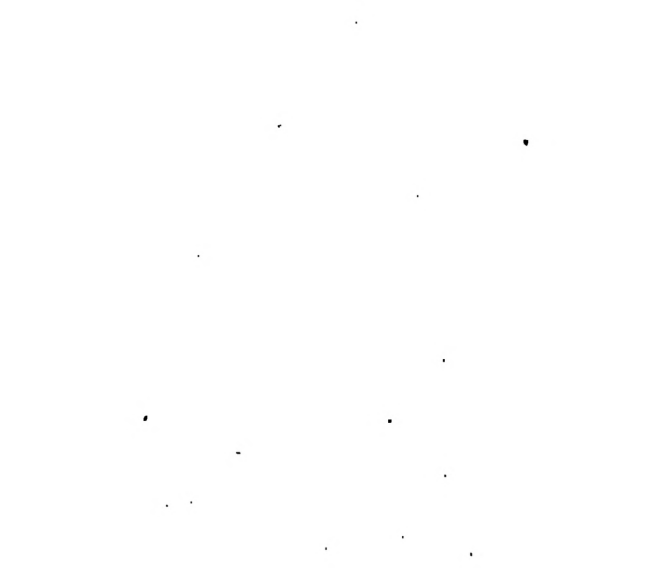
PREFACE

IN this volume the processes are given for the sake of clearness in as direct a statement as possible without regard to literary style. Explanatory notes have been introduced where they are most required for the benefit of beginners, but are as subdued as possible so as not to worry the experienced reader who may wish to omit them. For the benefit of beginners various gravimetric and volumetric estimations, hints on apparatus, etc., have been introduced at the beginning in greater detail than the description of analyses which follow and which are usually undertaken after considerable experience has been gained. In selecting processes, due regard must be paid to whether the analyses are for technical or commercial purposes.

In the case of commercial analyses where a large sum of money may be involved, select the most accurate methods every time, whereas in the technical analyses, the process must be selected with due regard to the time at the disposal of the chemist, combined with a fair degree of accuracy and the least expense, for the chemical department, like all the other departments of a factory, must be run with due regard to the cost of labour and materials.

The processes given have stood the test of actual practice, and, apart from the rare metals, will be found to cover any of the alloys usually manufactured in non-ferrous alloy factories. The object aimed at, has been to present a reliable guide to chemists professionally interested in the manufacture and use of alloys of this class, and to give in as concise a form as possible information which hitherto has been scattered throughout various text books. The results of typical analyses, Chapter XII., have been in most cases obtained by the processes given in this volume, but in a few instances have been obtained from standard text books.

J. R. D.



THE CHEMISTS' MANUAL OF NON-FERROUS ALLOYS

CHAPTER I

LABORATORY AND FITTINGS

THE laboratory should consist of at least two compartments, the workroom and the balance-room. The workroom should have benches around the walls as far as possible; a convenient bench being 3 ft. 3 ins. high and 2 ft. 6 ins. wide, with gas brackets fitted all round at convenient distances. A useful bench polish may be made by mixing together equal quantities of boiled linseed oil and methylated spirits, and applying regularly for some time till a fine glossy surface has been acquired. If this is done, it will be found that the benches may be kept perfectly clean and free from dust with a minimum of labour.

In one corner of the workroom is placed a sink, with a drainer on either side, and in another convenient corner a fume chamber, with either a good natural draught or forced draught, should be erected. A totally enclosed chamber with sliding glass windows is advisable.

This chamber is also fitted with 6 or 8 gas jets, to one of which is fitted a ring burner (Fig. 1), upon which is placed a steel plate of convenient size. A space on the bench, preferably in front of a window, should be reserved for titrations.

Shelves should be arranged around the walls, at a convenient height, for the chemicals in use, which should

be stored as far from the sink as possible. Cupboards should be fixed underneath the benches for the stock of chemicals and all apparatus not in use. If the apparatus when not in use is cleaned and stored away at once, the expenses for breakages will be considerably diminished.

Drawers should also be fitted in the benches to contain capsules, filter papers, test papers and other small accessories.

Balance-room.

The balance-room may be conveniently arranged thus. The balance-table, which should be perfectly rigid and

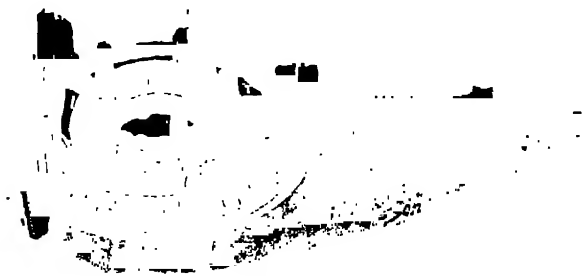


FIG. 1.

free from vibration, is placed in such a position that a good light falls on the balance. If a single compartment for balance-room and laboratory office is used, the desk and bookcase containing works of reference should be placed at the opposite side away from the balances.

There are so many excellent balances on the market at the present time that it is inadvisable to state any particular make, but hints on the purchase and care of a balance will be given in the following chapter.

Samples.

Samples under examination should be stored on shelves in the balance-room and when the examination is

completed should be carefully labelled with dates and report numbers, and placed on shelves in the laboratory specially set apart for this purpose. A useful label for this purpose is:—

No. 247.

Sample of Gunmetal.

From third cast, 6th January, 1919.

Received in laboratory (date) 6th January, 1919.

Examined by J.R.D.

Reported (date) 10th January, 1919.

Report No. 326.

File No. 29.

Sampling Compartment.

If a third room is available it should be reserved as a sampling compartment. If not, a space in the workroom,

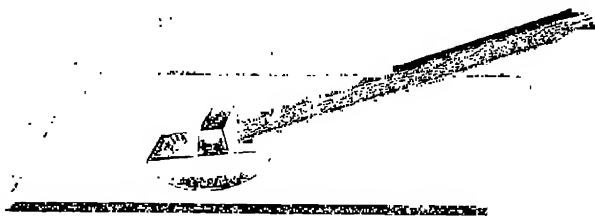


FIG. 2.

preferably partitioned off, should be set aside for this purpose.

A steel grinding plate (Fig. 2) is fixed up, alongside of which is placed a bench to contain the necessary sieves (Fig. 3), sample cloths, and other necessary sampling tools and cleaning apparatus.

On another bench is fitted a drilling machine (Figs. 4 and 5), placed in a convenient position for taking in pigs, ingots, or small castings. The drill itself must be kept scrupulously clean and must be used without oil. It is



FIG. 3.

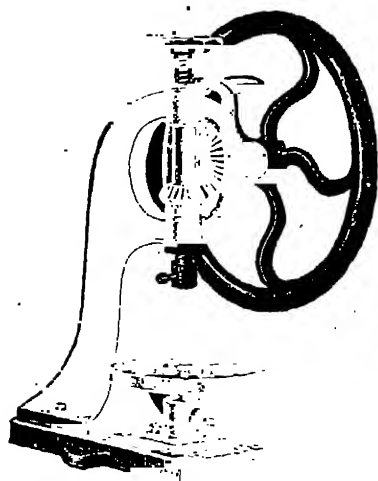


FIG. 4.—Hand Drilling Machine.

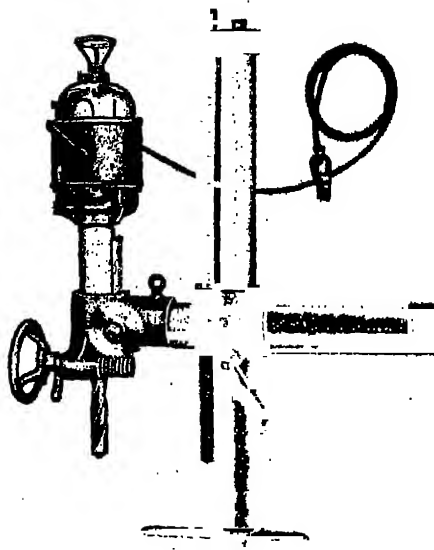


FIG. 5.—Electrical Drilling Machine.

advisable to remove the drill after each sample has been drilled and inspect it carefully as some particles of the previous sample may be left adhering to the drill, especially in the case of Bearing Metal samples and Lead Base Alloys. Cleanliness in the sample-room is absolutely the first consideration.

CHAPTER II

BALANCE AND WEIGHTS

Balance (Fig. 6).

(1) A balance bearing 70 to 80 grams in each pan usually suffices.

(2) It should be enclosed in a glass case to protect it from dust.

(3) The pans should not approach too near the sides of the case.

(4) It must admit of being opened and shut with facility.

(5) The pans must be provided with rests, in order to keep the pans immovable while the weights are being placed on the scales.

(6) The beam must also be supported so that the knife-edges are completely free from the supports while the balance is not in action, and the operator must be able to control the pan rests and beam without opening the balance.

(7) The balance should be provided with a pointer to mark the oscillations on a graduated arc.

(8) The balance must be provided with a spirit level and placed on three or four adjustable screws in order to have the balance absolutely level.

(9) A screw ought to be placed on either end of the beam for adjustment purposes, in order to regulate the centre of gravity.

After the balance has been accurately adjusted a good

chemical balance should be sensitive to one-tenth of a milligram.

It should be noted that the mere pointing of the index



FIG. 6

to zero is not sufficient evidence of equilibrium, but the pointer must oscillate equally on both sides of zero.

The pointer should swing equally on either side no matter whether with 10 grams on either pan, or with

50 grams, as is also the case when the weights are interchanged.

Before accepting the adjustment of the balance as accurate, try setting the balance in motion several times. A good balance will invariably assume its equilibrium.

Weights (Fig. 7).

A set of weights ranging from 50 grams to 1 milligram, which should be kept in a closed case with a compartment

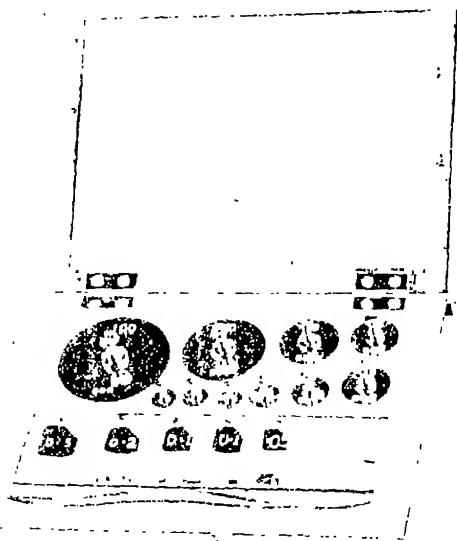
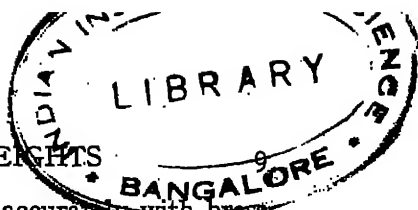


FIG. 7.

for each weight, will be found to be sufficient. Each weight should be distinctly marked and should only be touched with forceps.

The weights should be tested accurately to see that they agree among themselves; a convenient method is as follows :—

BALANCE AND WEIGHTS



A one-gram weight is balanced accurately with brass clippings. The original gram weight is removed and replaced with another gram weight. The counterpoise must still remain true. The third gram weight is similarly treated. The two-gram weight is then balanced against two of the tested one-gram weights, the five-gram weight is tried against the two-gram and the three one-gram weights, and so on.

The fractions of the gram are compared with one another in a similar manner and are finally compared with the gram weight. If the weights are correct in relation to one another the counterpoise in each of the above cases, and in all similar cases of nominally equal values, should be absolutely true. If the weights are incorrect they should be returned to the maker for readjustment.

The milligrams are usually determined by means of a centigram rider placed on the beam, which should be accurately graduated to one-tenth of a milligram.

Never weigh directly on the pan of the balance, it is always advisable to have an accurately balanced watch-glass on which to place the substance to be weighed.

The watch-glass may be balanced by means of a watch-glass on the opposite pan. It is unusual to obtain watch-glasses of exactly equal weights, but by means of a file the two nearest glasses may be exactly counterpoised. A piece of brass, nickeloid, or gunmetal may also be turned down to almost the counterpoise and finished exactly by means of a fine file.

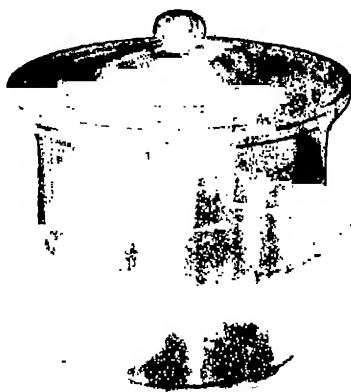


FIG. 8.

It is advisable to have a dish containing calcium chloride inside the case to absorb atmospheric moisture.

Never weigh a substance which is above the room

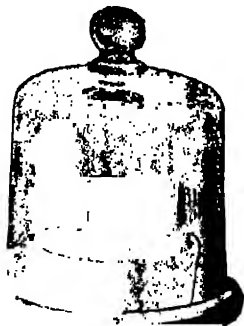


FIG. 9.



FIG. 10.

temperature. Allow to cool in a desiccator first (Figs. 8 and 9), and always weigh substances which are liable to absorb moisture from the atmosphere in a weighing bottle (Fig. 10), fitted with a light, ground-glass stopper.

CHAPTER III

CHEMICALS

It is always advisable, although "chemically pure" chemicals have been ordered, to conduct tests as to the freedom of these chemicals from the elements sought or other interfering elements. For instance, the Author has found so-called chemically pure iron perchloride containing traces of arsenic and phosphorus. Calcined magnesia and lime used for the estimation of sulphur in coke was also found to contain sulphur, and in caustic soda he has found traces of alumina. As each of the above chemicals was purchased from a reputable firm, the tests mentioned are advisable, and the results should be noted on the bottle or container thus :—

Calcined magnesia.

1 gram contains .0031 gram S.

In chemicals used for volumetric assays the impurities, as a general rule, only interfere with the keeping properties of the standard solution, and a blank experiment to find the factor must be frequently performed.

Chemicals should be stored in bottles or jars, either stoppered or with tightly fitting corks. They should never be allowed to lie about in paper parcels.

In pouring solutions from bottles, always hold the label side up, otherwise any drops running down the side of the bottle might obliterate the labels.

A useful arrangement of 16-oz. bench bottles containing

solutions in common use, should be kept on a shelf conveniently placed behind the working bench.

Hydrochloric acid	Sodium hydrate
Nitric acid	„ chloride
Sulphuric acid	Ferric chloride
Acetic acid	Methylated spirits
Tartaric acid	Litmus
Oxalic acid	Methyl orange
Ammonia	Phenolphthalein
Ammonium chloride	Mercuric chloride
„ sulphide	Stannous chloride, with a small
„ oxalate	piece of tin added
„ molybdate	1 per cent. methylene blue
„ nitrate	Starch solution.

The following is a complete list of reagents mentioned in the various processes given, and a judicious selection, in convenient quantities, must be made according to the processes to be adopted :—

Name.	Formula.	Name.	Formula.
Acid Acetic	$C_2H_4O_2$	Ammonium Phosphate	$(NH_4)_2HPO_4$
„ Arsenious	As_2O_3	„ Sulphide	$(NH_4)_2S$
„ Boric	H_3BO_3	„ Sulphocyanide	NH_4CNS
„ Citric	$C_6H_8O_7$	„ Vanadate	NH_4VO_3
„ Hydrochloric	HCl	Aluminium, Sheet	Al
„ Hydrofluoric	HF	Antimony, Pure	Sb
„ Nitric	HNO_3	Asbestos	—
„ Oxalic	$H_2C_2O_4$	Barium Carbonate	$BaCO_3$
„ Phosphoric	H_3PO_4	„ Chloride	$BaCl_2$
„ Sulphuric	H_2SO_4	„ Hydrate	$Ba(OH)_2$
„ Sulphurous	H_2SO_3	Bismuth, Pure	Bi
„ Tartaric	$C_4H_6O_6$	„ Nitrate	$Bi(NO_3)_3$
Ammonia	NH_4OH	Bromine	Br
Ammonium Acetate	$NH_4C_2H_3O_2$	Calcium Carbonate	$CaCO_3$
„ Carbonate	$(NH_4)_2CO_3$	„ Chloride	$CaCl_2$
„ Chloride	NH_4Cl	Carbon Bisulphide	CS_2
„ Molybdate	$(NH_4)_2MoO_4$	Cerium Chloride	$CeCl_3$
„ Nitrate	NH_4NO_3	Cinchonine	$C_{10}H_{11}NO$
„ Oxalate	$(NH_4)_2C_2O_4$	Cobalt Chloride	$CoCl_2$
„ Persulphate	$(NH_4)_2S_2O_8$	„ Nitrate	$Co(NO_3)_2$

Name.	Formula.	Name.	Formula.
Copper Chloride	CuCl_2	Potassium Chlorate	KClO_3
" Foil	Cu	" Chromate	K_2CrO_4
" Turnings	Cu	" Cyanide	KCN
" Sulphate	CuSO_4	" Ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$
Dimethylglyoxime	$\text{C}_2\text{H}_{12}\text{O}_{12}\text{N}_4$	" Ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6$
Ether	$\text{C}_2\text{H}_5\text{O}$	" Hydrate	KOH
Ferric Chloride	Fe_2Cl_6	" Iodide	KI
Ferrous Ammonium	$\text{FeSO}_4(\text{NH}_4)_2$	" Nitrite	KNO_2
" Sulphate	SO_4	" Permanganate	KMnO_4
Ferrous Sulphate	FeSO_4	" Thiocyanate	KSCN
" Sulphide	FeS	" Thiocarbonate	KCS_2
Glass Wool	—	" Titanic-Fluoride	K_2TiF_6
Hydrogen Peroxide	H_2O_2	Resorcinol	$\text{C}_6\text{H}_4(\text{OH})_2$
Iodine	I_2	Silver Nitrate	AgNO_3
Iron (flower wire)	Fe	Sodium Acetate	$\text{NaC}_2\text{H}_3\text{O}_2$
Iron Alum	$\text{K}_2\text{SO}_4\text{Fe}_2(\text{SO}_4)_3$	" Bicarbonate	NaHCO_3
Lead Acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	" Bismuthate	NaBiO_3
" Foil	Pb	" Bitartrate	$\text{NaHC}_4\text{H}_4\text{O}_6$
" Nitrate	$\text{Pb}(\text{NO}_3)_2$	" Carbonate	Na_2CO_3
" Oxide	PbO_2	" Chloride	NaCl
" Sulphate	PbSO_4	" Hydrate	NaOH
Lime, Slaked	$\text{Ca}(\text{OH})_2$	" Hypochlorite	NaOCl
Litmus	—	" Hyposulphite	$\text{Na}_2\text{S}_2\text{O}_3$
Logwood Chips	—	" Nitroprusside	$\text{Na}_2\text{NoFeCu}_2$
Magnesium Chloride	MgCl_2	" Peroxide	Na_2O_2
" Phosphate	MgP_2O_7	" Phosphate	NaH_2PO_4
Manganese Nitrate	$\text{Mn}(\text{NO}_3)_2$	" Salicylate	$\text{NaC}_7\text{H}_5\text{O}_2$
" Dioxide	MnO_2	" Sulphide	Na_2S
Marble Chips	CaCO_3	Stannous Chloride	SnCl_2
Methylated Spirits	$\text{C}_2\text{H}_5\text{OH}$	Starch	$\text{C}_6\text{H}_{10}\text{O}_5$
Methylene Blue	$\text{C}_{16}\text{H}_{18}\text{NO}_2$	Tannic Acid	—
Methyl Orange	—	Thymol	$\text{C}_{10}\text{H}_{14}\text{O}$
Mercuric Chloride	HgCl_2	Tin, Pure	Sn
Mercurous Nitrate	HgNO_3	Titanic Oxide	TiO_2
Molybdic Acid	H_2MoO_4	Tungsten Oxide	WO_3
Nickel, Pure	Ni	Turmeric	—
" Sulphate	NiSO_4	Uranium Acetate	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$
Nitroso-B-Naphthol	$\text{C}_{10}\text{H}_7(\text{OH})\text{NO}$	" Nitrate	$\text{UO}_2(\text{NO}_3)_2$
Phenolphthalein	$\text{C}_{20}\text{H}_{14}(\text{OH})\text{CO}_2$	Vanadium Oxide	V_2O_5
Potassium Anti-	$\text{KC}_2\text{H}_3\text{O}_4$	Zinc, Powdered	Zn
mony Tartrate	$(\text{SbO})_4$	" Granulated	Zn
" Bichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	" Chloride	ZnCl_2
" Bisulphate	KHSO_4	" Sulphate	ZnSO_4
" Carbonate	K_2CO_3		

APPARATUS

Pipettes (Fig. 11).

Pipettes should be standardized according to the method of manipulation adopted by the operator.

Suppose the operator follows no fixed rule, simply letting the fluid run out in one instance, or letting it drain afterwards, or, in a third instance, blowing out the last particles, the quantity of fluid cannot be equal in each case.

A reliable method is to allow the fluid to run out, count ten seconds, and dip the tip of the pipette three times. All pipettes should be standardized in the following manner.

On the neck of the pipette gum a small strip of paper, overlapping the mark both top and bottom. Fill the pipette exactly to the mark with distilled water at 15.5° C. and run a weighed beaker in the manner to be adopted generally as previously described. The pipette is pronounced correct if the number of c.c.s. weigh exactly the same number of grams. Suppose a pipette delivered 50.06 grams, draw a thin line on the paper slightly below the mark, and weigh the contents once more. Continue this process till the contents weigh

exactly the same number of grams as indicated. Then, with a file, mark on the neck of the pipette a ring corresponding exactly to the corrected mark obtained on the paper. Pipettes should be thoroughly cleaned and put away after use.



FIG. 11.

Burettes (Figs. 13-14).

Burettes should be graduated to $\frac{1}{10}$, or even $\frac{1}{20}$ c.c., and are usually found to be accurate as purchased, or a correction may be supplied with the burette. For clear solution, the author finds a burette with a milk scale back ground, through which runs a blue line vertically, to be excellent, refraction causing the liquid to appear pointed, and for solutions, such as iodine, etc., an Erdmann's float (Fig. 12) is advantageous. The blue-lined milk scale burette shows a distinct point at the number of c.cs. and must be held level with the eye, when reading. In reading a plain burette without a float always suspend it so that the bottom of the meniscus on the liquid is on a level with the eyes.

The stopper should be lightly vased, and the burette should be cleaned immediately after use.

Before filling the burette with standard solution always rinse it with a few c.cs. of the standard, otherwise spots of water adhering to the walls of the burette will dilute the standard, with the consequence that false results will be obtained.

Desiccator.

The desiccator should be air-tight, and the desiccating agent used, may be either calcium chloride or



FIG. 12.



FIG. 13.



FIG. 14.

concentrated sulphuric acid.

The ground-glass rim of the desiccator should be lightly vaselined.

Kipp's Apparatus (Fig. 15).

This apparatus is used for generating the carbonic acid gas and sulphuretted hydrogen gas so frequently mentioned in the following processes.



When fitted up for use, there should be absolutely no escape of gas, and all ground-glass fittings should be lightly vaselined.

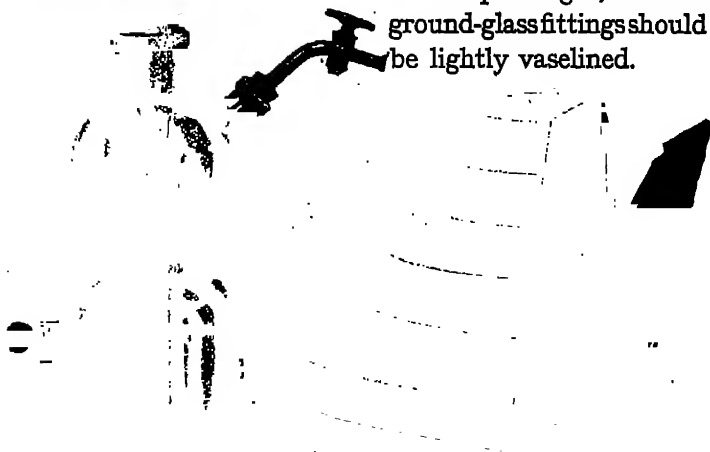


FIG. 15.

FIG. 16.

For carbon di-oxide use marble chips and dilute hydrochloric acid, and for sulphuretted hydrogen use ferrous sulphide and dilute sulphuric acid.

The stock of filter papers should be stored in a drawer which is absolutely dry and water-tight, and a convenient case for those in daily use is shown in Fig. 16.

DRYING OVENS.

Water baths or drying ovens (Figs. 17, 18).

Care must be taken that the water in the jacket never falls below a certain mark, gauges being usually affixed for this purpose. A condensing apparatus is often attached, as shown in Fig. 18, and will be found to be most convenient. Fig. 17 shows an ordinary water bath with water level and run-off tap attached.

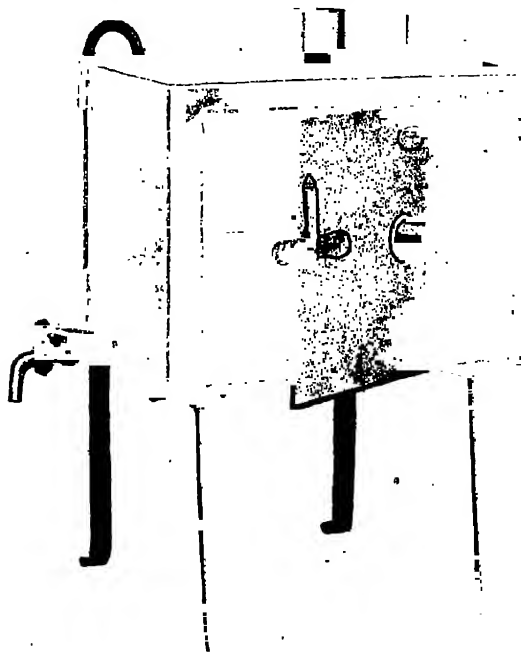


FIG. 17.

Wash bottle fittings should be made in the laboratory, and a few hints on bending tubes, etc., are appended (Fig. 19).

To bend Glass Tubing.

Heat the tube in the broad flame of an ordinary fish-tail burner till it begins to bend with its own weight,

then it may be bent to the requisite shape without creasing on removing from the flame.

To draw a Tube out to a Jet.

Heat the glass in the blowpipe flame at the point where the jet is required, while slowly turning it round until it thickens. When heated equally all round, withdraw it from the flame and draw it out to the required

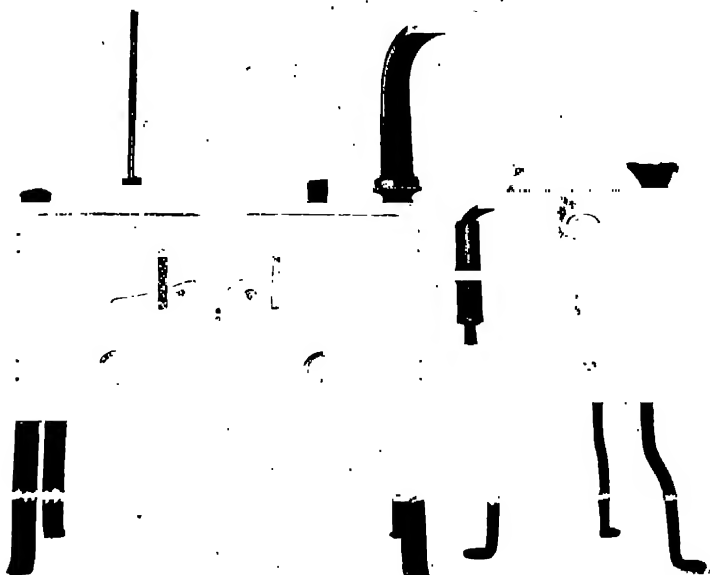


FIG. 18.

jet. Cut off where required, and heat the end in the flame for a moment to remove the sharp edges.

To cut Glass Tubing.

Nick the tube with the sharp edge of a three-cornered file, place the thumbs, one on each side of the nick, give a quick movement as if to bend the tube, when it easily breaks off.

To grind Glass.

The ends of thick tubes may be ground level upon a stone with turpentine.

The addition of sand or emery powder increases the action.

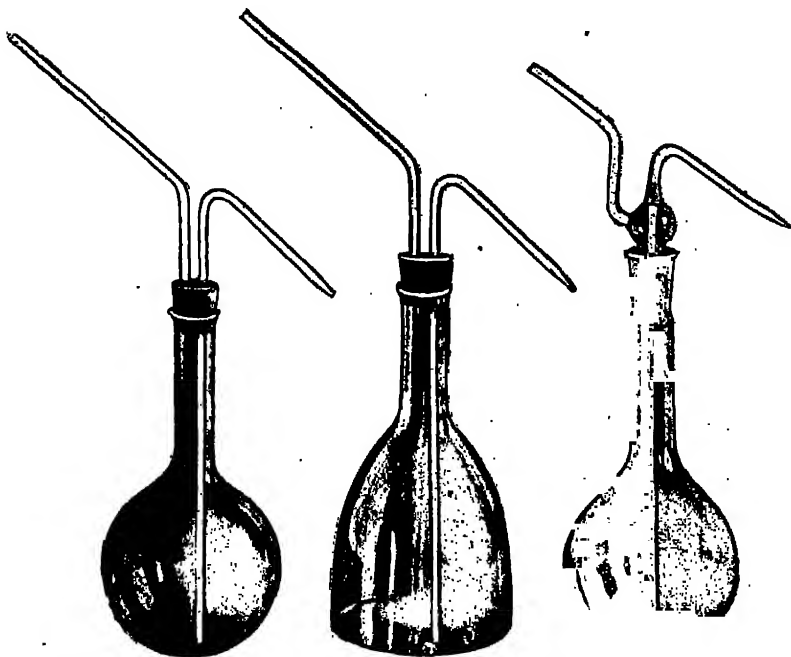


FIG. 19.

To fuse Platinum or Nickel Wire into a Tube.

Draw the end of the tube to a jet and insert the clean dry wire. Heat the end of the tube in the flame till the glass fuses and clasps the wire. Cool slowly.

To remove Fixed Stoppers.

Heat the neck of the bottle by pouring hot water round it, or rotating once quickly in a flame. This

expands the neck and allows the stopper to be withdrawn.

Tap the stopper gently with a wooden object till it is loosened. Sometimes a stopper may be removed by placing the flat part of the stopper in the crevice of a door and turning the bottle gently.

Stoppers may also be removed by placing a little oil round them, which, on standing some time, sinks in and loosens the stopper.

A list of apparatus for quantitative analyses described in this volume is as follows.

Sample-Room.

Crusher with hammers, trowels, spatulas, mixing cloths, sieves, brushes, etc.

Sample tins and bottles.

Mortars—iron, wedgwood, and agate.

Drilling machine with drills.

Balance-Room.

Balance, weights, and bridge for specific gravities, brushes, weighing glasses, weighing bottles, desiccator, spatulas (steel and bone or ebonite), dusting and cleaning materials.

Work-Room.—Volumetric Analysis.

Burettes—50–25–10 c.cs., burette stands.

Floats, pipettes—100–50–25–20–5 c.cs., pipette stand.

Graduated flasks—1000–500–250–200–100 c.cs. (Fig. 20).

Graduated measures—100–50–25–20–10 c.cs. (Fig. 21).

Porcelain spotting plates.

Hydrometer and glasses, thermometers, Nessler's colour tubes or colorimeter tubes.

Colorimeter.

Gravimetric Analyses.

Platinum wire in holder.

Nickel " "

Kipp's apparatus.

Beakers, 500, 300, 200, 100 c.c. capacity.

Boiling flasks, 750-500-250- c.c. capacity.

Liebig's condenser or worm condenser.

Two-holed rubber corks.

Glass rods and tubes.

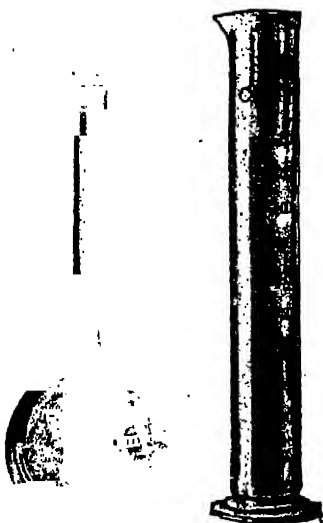


FIG. 20.

FIG. 21.

FIG. 22.

Wash bottles, rubber tubing, and gas tubing.

Porcelain basins (various).

„ capsules (various).

„ lids for capsules.

„ „ Rose's, with tubes.

Platinum capsules.

„ crucible, with lid.

Test tubes and stand.

Filter stands.
Ring burner and plate.
Bunsen, Techn, and Argand burners (Figs. 22, 23, 24).
Foot blowpipe.
Crucible tongs, tripod stands, wire gauze and triangles.
Water baths.
Filter papers (various sizes and degrees of fineness),
filter-paper holder.
Filter funnels (preferably ribbed), various sizes.
One set bench bottles, narrow mouthed, 16 oz.

FIG. 23.



FIG. 24.

One set chemical bottles, various sizes, wide mouthed.
Bottle labels. It is advisable after applying labels
to coat them with wax or clear varnish.

Wash bottle, flasks (fitted as in Fig. 19).

One bottle should be labelled and reserved for the
following solutions :

Water, cold.

„ hot.

Nitric acid water (1-10).

Ammonia water (1-5).

Methylated spirits water (1-6).

Ammonium chloride (2 per cent.).

„ acetate (1.08 sp.gr. with 10 c.c. acetic acid per 500 c.c.).

Muffle furnace (Fig. 25).



FIG. 25.

Fletcher furnace, with tubes closed at one end, also tubes open at both ends.

Set carbonic acid absorption bulbs, nitrogen bulbs.

„ calcium chloride tubes.

Calorimeter.

CHAPTER IV

DETECTION OF METALS

Aluminium.—With ammonia gives a white gelatinous precipitate. Oxide strongly heated on charcoal with cobalt nitrate, a bright blue mass is obtained.

Antimony.—Hydrogen sulphide in acid solution produces a characteristic orange red precipitate.

Heat a small quantity in the reduction zone of a bunsen, the flame is given a blue tinge and a basin with cold water held above it receives a black deposit of antimony. This is insoluble in sodium hypochlorite (distinction from arsenic).

Arsenic.—Flame deposit test as above. Deposit soluble in sodium hypochlorite. Add concentrated hydrochloric acid and a few drops of stannous chloride in hydrochloric acid. On heating the solution turns brown, then black.

Bismuth.—In a neutral solution, potassium bichromate gives a yellow precipitate insoluble in caustic soda (distinction from lead).

Ammonium carbonate produces a white precipitate.

Cadmium.—With hydrogen sulphide a yellow precipitate is produced, insoluble in ammonium sulphide or caustic alkalis.

Calcium.—Ammonium oxalate added to an ammoniacal solution produces a white precipitate.

Moistened with hydrochloric acid on a platinum wire gives a red flame test.

Chromium.—Caustic soda gives a green precipitate with chromic salts. The yellow colour of normal chromates becomes red on the addition of acid.

Cobalt.—Ammonium sulphide produces a black precipitate insoluble in acetic acid and weak hydrochloric acid. Ammonium sulphocyanide produces a beautiful blue colour.

Copper.—Azure blue colour produced on the addition of ammonia destroyed with cyanide of potash. Hydrogen sulphide does not produce a precipitate in the decolorized solution.

Iron.—Potassium ferricyanide produces a dark blue precipitate with ferrous salts, and ammonium sulphocyanide produces a blood red colour or precipitate with ferric salts.

Lead.—Sulphuric acid produces a white precipitate soluble in ammonium acetate. In neutral solutions potassium chromate produces a yellow precipitate soluble in caustic soda (distinction from bismuth).

Magnesium.—Ammonium chloride, ammonia and sodium phosphate produce a white precipitate on stirring.

Manganese.—Ammonium sulphide produces a flesh-coloured precipitate.

Traces of manganese, on boiling with nitric acid and sodium bismuthate, produce a violet-red colour.

Molybdenum.—A hydrochloric acid or a sulphuric acid solution to which stannous chloride is added, turns blue, then green and finally brown.

In the presence of acetic acid (not mineral acid) pyro gives a sensitive orange colour.

Nickel.—Dimethylglyoxime produces a greenish precipitate. Ammonium sulphide produces a black precipitate soluble in excess forming a dark-coloured solution.

Silver.—Hydrochloric acid produces a curdy white precipitate, soluble in ammonia, reprecipitated with

nitric acid. With arsenates a red precipitate is produced, insoluble in ammonia.

Tin.—Stannous salts give a white precipitate with mercuric chloride.

Titanium.—In hydrochloric acid solutions a piece of tin produces a violet colour.

Sulphate solution produces an orange-red colour with hydrogen peroxide.

Tungsten.—Evaporate to dryness with hydrochloric acid—nitric acid (4-1) dilute with hydrochloric water (1-3) and add metallic tin, zinc, or aluminium, a blue colour is produced which disappears on copious dilution.

Uranium.—Potassium ferrocyanide produces a brown precipitate or brown-red colour.

Vanadium.—Hydrochloric acid solutions assume a blue colour on the addition of zinc, distinguished from copper blue by being undestroyed by iron.

Zinc.—Ammonium sulphide produces a white precipitate, and potassium ferrocyanide produces a white precipitate.

PRELIMINARY TESTS.

A qualitative examination is advisable before deciding on the full scheme of analysis.

Treat the alloy with nitric acid, boil and allow any precipitate to settle and filter. Preserve the filtrate.

Treatment of Precipitate.

Silicon.—Boil with hydrochloric; any precipitate will consist of silicon; filter off precipitate.

Antimony.—Add a piece of bright copper foil; black deposit on the foil indicates the presence of antimony.

Tin.—Add metallic granulated zinc which precipitates in, if present, in the metallic form, precipitates oxides to a white powder on the addition of nitric acid.

Treatment of Filtrate.

Pass sulphuretted hydrogen gas through the filtrate, precipitate may consist of lead, copper, bismuth, cadmium, or arsenic. Filter and preserve the filtrate.

Redissolve the precipitate in nitric acid and filter off sulphur if necessary.

Lead.—Add sulphuric acid and boil, white precipitate indicates lead. Filter off precipitate.

Copper.—Add ammonia, blue colour indicates the presence of copper ; add potassium cyanide to destroy the blue colour and add ammonium sulphide. Black precipitate indicates bismuth and yellow precipitate cadmium and arsenic. The yellow colour may be masked by the black colour of the bismuth. Filter off the precipitate, redissolve in nitric acid.

Bismuth.—Add carbonate of ammonium which precipitates bismuth as a white precipitate. Filter off, if found.

Arsenic.—Add magnesia mixture which precipitates arsenic as a white powder.

Cadmium.—To the filtrate from arsenic add ammonium sulphide. A yellow precipitate is produced if cadmium is present.

Treatment of Filtrate from H_2S Metals.

Boil off H_2S and add sulphurous acid, and add ammonia ; any precipitate consists of chromium and aluminium. Filter and preserve the filtrate.

Chromium.—Redissolve in hydrochloric acid, reduce with sulphurous acid and add caustic soda. Greyish-green precipitate indicates chromium. Filter off.

Aluminium.—Acidify the filtrate from chromium with hydrochloric acid, oxidize with a few drops of nitric, boil and add excess of ammonia. Flocculent precipitate indicates aluminium.

Treatment of the Filtrate from Chromium and Aluminium.

Boil off sulphurous acid and oxidize with bromine water. Add ammonia, and any precipitate consists of iron and manganese.

Dissolve precipitate in hydrochloric acid, neutralize with ammonia.

Iron.—Add ammonium acetate. Brown precipitate indicates iron. Filter off iron.

Manganese.—Add bromine water and ammonia; a white precipitate rapidly turning brown indicates manganese.

Treatment of the Filtrate from Iron and Manganese.

Filtrate may contain nickel, cobalt, or zinc.

Nikel.—Add dimethylglyoxime; any precipitate will consist of nickel. Filter off precipitate.

Cobalt.—Acidify the filtrate with acetic acid and add potassium nitrite. Yellow precipitate indicates cobalt. Filter off precipitate.

Zinc.—Add ammonia to the filtrate from cobalt and add ammonium sulphide. White precipitate indicates zinc.

SPECIAL SOLUTIONS AND GASES REQUIRED.

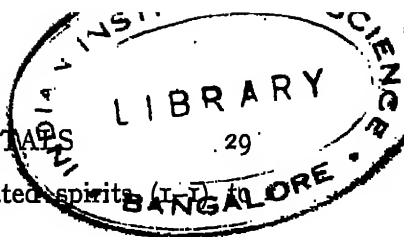
LITMUS SOLUTION.—The sensitive violet-coloured constituent of litmus may be separated from the other colouring matters and gums by heating with dilute sulphuric acid (4 per cent.), when it is precipitated in the form of a sulphonic acid. Collect and wash.

Redissolve in boiling water, neutralize with caustic soda, when an exceedingly sensitive violet solution is obtained.

Red with acid. Blue with alkali.

METHYL ORANGE.—Dissolve in a little alcohol and

DETECTION OF METALS



dilute with distilled water, methylated spirits (1-2) in 1 litre.

Red with acids. Yellow with alkalis.

PHENOL PHTHALEIN.—Dissolve in alcohol and dilute with distilled water, methylated spirits (1-1).

Colourless with acids. Red with alkalis.

No good for ammonia or in the presence of CO_2 .

AMMONIUM SULPHIDE (Yellow).—In ammonia water (1-2), suspend some flowers of sulphur and pass H_2S gas to saturation. Filter into a tightly stoppered bottle.

MAGNESIA MIXTURE.—Dissolve 66 grams magnesium chloride in 250 c.cs. water and 150 grams ammonium chloride in 400 c.cs. water, add 200 c.cs. ammonia and make up to 1 litre.

Solution used for the precipitation of arsenic and phosphorus.

AMMONIUM MOLYBDATE.—A specially prepared nitric acid solution of ammonium molybdate is made as follows. Dissolve 80 grams molybdic acid in 80 c.cs. ammonia (880) and pour quickly into 300 c.cs. nitric acid and 300 c.cs. water, stirring all the time and keeping as cool as possible. Make up to 1 litre, allow to stand over night, decant the clear liquor into a stoppered bottle. Keep in a cool place and store away from the light.

AMMONIUM ACETATE.—100 grams ammonium acetate, 8 c.cs. glacial acetic acid made up to 1 litre.

SULPHURETTED HYDROGEN GAS.—Usually generated in a Kipp's apparatus, sulphide of iron and a dilute solution of sulphuric acid being used.

CARBON DIOXIDE GAS.—Usually generated in a Kipp's apparatus, marble chips and dilute hydrochloric acid being used.

SULPHUR DIOXIDE GAS.—Usually generated in a boiling flask; copper turnings and strong sulphuric acid being used and gentle heat applied.

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BERRINGER'S SOLUTION FOR ARSENIC DISTILLATIONS.—Dissolve 400 grams CaCl_2 and 200 grams of Fe_2Cl_6 in 200 c.cs. distilled water, cool and add 400 c.cs. hydrochloric acid. Dilute to 1 litre. Use 75 c.cs. of this solution for each distillation.

DIMETHYLGLYOXIME.—Dissolve 40 grams dimethylglyoxime in 1 litre of methylated spirits. 10 c.cs. of this solution will precipitate 1 gram of nickel.

CHAPTER V

GRAVIMETRIC ESTIMATIONS

It is absolutely indispensable that the forms into which bodies are converted for the purpose of estimation by weight, should be of a known composition and should be capable of being accurately weighed. In precipitating substances in a known form where slight excess is mentioned, care must be taken that only 2 or 3 drops of the precipitant more than absolutely necessary to precipitate the substance in that form, are added, large excess means that 20 or 30 c.cs. additional should be used.

In filtering the precipitate great care must be taken that the last particles of precipitate are removed from the vessel and transferred to the filter. For this purpose a glass rod with a policeman is recommended, *i.e.* a rod with about 1 inch of tight-fitting rubber tubing attached. In washing the precipitate, the substance used as a precipitant must be thoroughly washed out, as, if it is non-volatile, the results will be too high, which errors, supposing 1 gram sample was used for the estimation, upon calculating to per cent., would be multiplied a hundred-fold. Therefore test the washings to ensure that they are completely free from the precipitant. In cases where the precipitates cannot be ignited, they are weighed in previously dried and weighed filter papers. Dry the filter paper in the water bath at 100° C. till constant in weight and weigh in a weighing bottle. Some chemists dispense with the weighing bottle and note the weight at the end of 1

minute, but the weighing tube is always preferable. Ignited precipitates should always be cooled to the temperature of the room in a desiccator previous to weighing. This is not absolutely necessary in every case, but it is always advisable, as the dust factor, which is apparent in some works' laboratories is thereby overcome.

Filter papers are now manufactured of such quality that the weight of ash is extremely minute, and most of the high-class manufacturers mark on each packet supplied the weight of ash. This weight should be deducted in each estimation before calculating to percentage.

SPECIFIC GRAVITY.

Solid substances heavier than, and insoluble in, water.
The substance is first weighed in air in the ordinary



FIG. 26.

manner. It is then suspended from the beam of the balance by a fine light hair or fibre. The weight of the substance is taken again while immersed in water (distilled) at 15.5°C. , care being taken that the surface of the substance is free from adherent air bubbles.

The removal of air bubbles may generally be effected by applying a camel's-hair brush to the surface of the solid after it has been immersed in water.

A convenient arrangement for weighing the substance is shown in the accompanying figure. A small wooden

bridge is placed over the left-hand scale of the balance. This bridge serves as a support for the beaker of distilled water. The suspending hair is hung from the second hook beneath the hook supporting the scale. The removal of the scale pan which might destroy the equilibrium of the balance is thus rendered unnecessary. The specific gravity of the substance is obtained by dividing the weight of the body in air by the loss in weight which it sustains in water.

Thus W = weight of solid in air.

W_1 = weight of solid in water at 15.5° .

$$\text{Then sp. gr.} = \frac{W}{W - W_1}$$

Example.—A piece of brass weighed 20.143 grams in air and 17.611 grams in water

$$\frac{20.143}{20.143 - 17.611} = \frac{20.143}{2.532} = 7.955 \text{ sp. gr.}$$

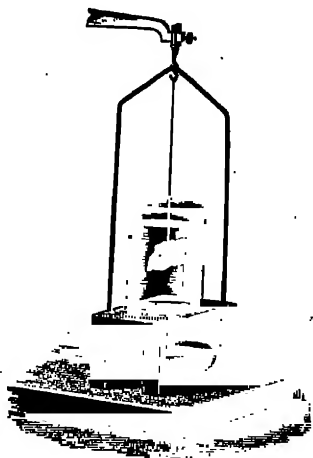


FIG. 27.—Weighing a Solid in Water.

1. LEAD AS SULPHATE.

To the solution containing the lead, add sulphuric acid, in slight excess, to precipitate the lead as PbSO_4 , boil and add methylated spirits, carefully at first, till the violent action due to the liberated nitrous fumes has abated. Add $\frac{1}{2}$ of the original bulk of the methylated spirits, boil gently, and allow to stand till the precipitate has completely settled. Filter through a Swedish filter paper and wash thoroughly with water containing $\frac{1}{2}$ of

its bulk of methylated spirits. Dry, separate the precipitate and ignite the paper first, in a weighed porcelain crucible. Some of the precipitate which adhered to the paper is reduced to metallic lead by the action of the organic matter in the paper. Allow to cool, add 2 drops of sulphuric acid and carefully drive off excess over a bunsen. Add the precipitate and continue the ignition till constant in weight. Cool and weigh. Factor = .68293 lead.

NOTE 1.—A porcelain capsule must be used, as this precipitate violently attacks all metallic capsules.

NOTE 2.—The capsule must be previously weighed, as it is impossible to brush out the precipitate.

2. LEAD AS CHROMATE.

If the solution is not distinctly acid, render it so with acetic acid, then add potassium bichromate in excess, and if free nitric acid is present, add acetate of soda in sufficient quantity to replace the free nitric acid by free acetic acid; let the precipitate settle at a gentle heat, collect on a weighed filter paper, wash thoroughly and dry in the water bath till constant in weight.

The precipitate may be ignited after separating from the paper and igniting the paper first, but in this case care must be taken that hardly any salt is left adhering to the paper, and also that the temperature of ignition is not too high. Factor = .64055 lead.

3. BISMUTH AS OXIDE.

Dilute the solution containing the bismuth to 200 c.cs., then add solution of ammonium carbonate in very slight excess and warm for a short time. Filter and wash with warm water. This precipitate is ignited apart from the paper, as described under Lead. Factor = .89677 bismuth.

PRECAUTIONS.

1. Neither chloride nor sulphate of bismuth must be present in the solution.

The bismuth if existing in these forms, is first precipitated as sulphide, filtered and the sulphide dissolved in hot dilute nitric acid.

2. It is necessary to guard against the addition of too great an excess of ammonium carbonate since bismuth carbonate is distinctly soluble in excess of this reagent.

4. COPPER AS OXIDE.

To the solution in which the copper is to be estimated, add slight excess of caustic soda and boil till the blue hydrated oxide of copper is turned into the black anhydrous oxide, leaving the supernatant liquid colourless when the precipitate settles. Wash the precipitate four times by decantation with hot water, decanting through a filter paper. Wash the precipitate on the paper and continue till the washings are not the least alkaline to litmus. Dry, ignite the paper first, and when completely ignited, add the precipitate and ignite till constant in weight. Factor = .798 copper.

PRECAUTIONS.

1. Ignite in a weighed capsule and cool in a desiccator before weighing.

2. The action of reducing gases must be carefully guarded against in the process of ignition.

3. About 1 gram sugar added to the solution before precipitation with caustic soda assists the reaction.

5. TIN AS SULPHIDE.

Dilute the solution to 200 c.cs. and if not already acid, add 10 c.cs. hydrochloric acid in excess. Through this solution pass H_2S gas to saturation and allow the

precipitate to settle in a warm place. Filter and wash thoroughly, dry and separate from the paper. Ignite the paper apart from the precipitate, moisten the ash with 2 drops of nitric acid and heat till the excess of acid is expelled. Cool and add the precipitate, cover the crucible with a lid and heat gently, remove the lid and continue heating till the smell of escaping sulphur dioxide is no longer perceptible and finish igniting at a red heat. Allow to cool, add a little powdered ammonium carbonate and ignite again strongly, which completes the removal of the sulphur. Cool, weigh and again treat with ammonium carbonate. Repeat this operation till constant in weight. Factor= $\cdot 78738$ tin.

A porcelain crucible must be used, as tin alloys with platinum.

6. TIN AS OXIDE.

In metallic samples, a weighed quantity is treated on a hot plate with nitric acid and water (1-2) till the tin has been thoroughly oxidized. Add 5 drops of saturated solution of mercuric chloride solution and evaporate to very small bulk. Take up with a few drops of nitric acid and 100 c.cs. water, boil and allow to settle. Filter through a Swedish filter paper, and proceed as directed in preceding process.

Separate the precipitate from the paper and ignite the paper first, afterwards adding the precipitate. Factor= $\cdot 78738$ tin.

7. ANTIMONY AS SULPHIDE.

To the antimony solution add hydrochloric acid, if not already present, then tartaric acid and dilute to 200 c.cs. Introduce the clear solution into an Ehrlenmeyer flask fitted with a two-holed indiarubber cork. Through one hole passes a tube bent outside at a right angle which extends nearly to the bottom of the flask, through the

other passes an exit tube which reaches only a short way into the flask. Through the first tube pass H_2S gas to saturation and while still passing the gas heat the flask, even to boiling. While moderately warm, pass CO_2 gas through the solution almost to the expulsion of H_2S . The heating of the solution tends to coagulate the precipitate. Filter rapidly through a weighed filter-paper and wash with water containing a little H_2S water and dry at $100^\circ C$.

Note the weight and take an aliquot part, and place in a weighed porcelain crucible with a lid. Moisten (gently at first) with a few drops of nitric acid (1.42 sp. gr.) keeping the crucible covered with the lid, as the action is violent at first, then just cover the precipitate with fuming nitric acid and evaporate to dryness on a water bath. Ignite gently at first, then raise the temperature to redness and continue heating till constant in weight.

From the weight of Sb_2O_4 thus obtained, the weight corresponding to the whole of the sulphide precipitate is calculated, and from this the percentage of antimony is obtained. Factor = .788 antimony.

8. ANTIMONY OXIDE.

In metallic samples a weighed quantity is treated on the hot plate with nitric acid water (1-2) till thoroughly oxidized, a few drops of mercuric chloride is added and evaporated almost to dryness.

Add a few drops of nitric acid, 100 c.cs. water, boil and allow to settle. Filter through a Swedish filter-paper, wash thoroughly, and proceed with the ignition as described under tin (PAR. 6). Factor = .788 antimony.

9. ARSENIC.

To the solution containing the arsenic add excess of ammonia, 10 c.cs. ammonium chloride and finally excess

of magnesia mixture, stir well and allow the precipitate to settle all night if possible. Collect the precipitate on a weighed filter-paper, wash well with ammonia water (1-5) and dry in the water bath till no further loss in weight is observed. Weigh as ammonium magnesium arseniate. Factor = .39473 arsenic.

This precipitate may be ignited and weighed by the following means:—

Separate the precipitate from the paper, drench the paper with ammonium nitrate solution and ignite gently in a weighed capsule till the paper has completely burned off. Now add the precipitate and ignite at a low heat till constant in weight. Weigh as magnesium arseniate. Factor = .48387 arsenic.

10. ARSENIC, MOLYBDATE METHOD.

To the solution containing the arsenic which must not contain phosphorus, add 10 c.cs. nitric acid and 10 c.cs. ammonium nitrate solution and evaporate to about 50 c.cs. bulk. Now add 50 c.cs. ammonium molybdate solution and allow to digest at a temperature between 70° and 80° C. for one hour. Filter through a weighed filter-paper, wash with nitric acid water (1-10) and dry in the water bath till constant in weight.

Arsenic Molybdate : : Arsenic : x

Factor = .06308 arsenic acid

= .04114 arsenic.

11. ARSENIC, DISTILLATION PROCESS.

A 20 oz. flask is fitted with a two-holed indiarubber cork, through one hole of which passes a stoppered funnel, which reaches only a short way into the flask. Through the other hole passes a tube bent twice, at right angles, which is fitted to a glass worm condenser, from the end of which is suspended a small glass funnel which just

dips under the surface of 100 c.cs. of distilled water, contained in a 300 c.c. beaker.

* Solution required is 10 grams ferric chloride, dissolved in 100 c.c. hydrochloric acid, in which has been dissolved as much copper foil as will dissolve by boiling.

Process.—Place the solution in which the arsenic is to be estimated in the flask, and make the connections. Fill the funnel with the above ferric chloride solution and run into it this solution, turn the stopper and distil the contents of the flask gently till $\frac{2}{3}$ of the bulk has been distilled over.

If the distillation is conducted gently, no ferric chloride will be distilled over. Add a little more of the ferric chloride solution and again distil gently as before. The arsenic in this distillate may be precipitated by the magnesia mixture or molybdate methods previously described, or may be treated directly volumetrically as will be subsequently described under Volumetric Estimations (PAR. 92).

12. IRON.

Iron is generally precipitated as hydrated ferric oxide, therefore about 10 c.cs. nitric acid must be added to the solution containing iron, and the whole boiled to bring the iron to the ferric state. Allow the solution to cool, and cautiously add a slight excess of ammonia, which precipitates all the iron as $\text{Fe}_2(\text{OH})_6$. Collect the precipitate on a good-sized filter paper, and wash thoroughly with boiling water, dry, ignite carefully and weigh as Fe_2O_3 . Factor = .700 iron.

13. IRON, ACETATE METHOD.

The solution is thoroughly boiled with 10 c.cs. of nitric acid to oxidize and is carefully neutralized with ammonia. This is best performed by adding ammonia, with constant

* An alternative solution by Berringer is given on p. 30.

stirring, as the brown precipitate which first forms takes some time to dissolve. When this point is reached, add the ammonia carefully, drop by drop, till only a faint precipitate or turbidity is produced which is just destroyed by adding a drop of hydrochloric acid. Bring this neutralized solution to the boil and add 3 c.c. of ammonium acetate solution (saturated) approximately for every .1 gram of iron present and continue boiling for 30 seconds. Filter off this precipitate and allow to drain thoroughly. Redissolve from the paper by means of hot dilute hydrochloric acid (1-3), wash the paper thoroughly, add 10 c.cs. nitric acid, boil, and proceed as directed in PAR. 12.

14. ALUMINA AS OXIDE.

To the solution containing the alumina add 10 c.cs. hydrochloric acid and a slight excess of ammonia, which produces a flocculent white precipitate of hydrated oxide of alumina. Boil off excess of ammonia, collect the precipitate on a filter-paper and wash well with hot water. Pour hot dilute hydrochloric acid (1-3) through the paper to dissolve off the precipitate and wash thoroughly with hot water. Reprecipitate with ammonia, boil off excess of ammonia, allow the precipitate to settle, filter, wash with hot water, ignite and weigh as Al_2O_3 . Factor = .533 aluminium.

NOTE 1.—It is advisable to test both filtrates for alumina, a little of which may have escaped precipitation.

NOTE 2.—If the ammonia is added to the solution containing the alumina while the latter is at a temperature of 15° to 20° C. and boiling subsequently, the precipitate will be more granular.

15. ALUMINA AS PHOSPHATE.

Dilute the solution containing the alumina to 250 c.cs., add 30 c.cs. ammonium phosphate solution and then

ammonia till a faint permanent precipitate is formed. Add 3 drops of hydrochloric acid and stir till the precipitate has dissolved and add 30 c.cs. sodium hyposulphite solution. The addition of sodium hyposulphite reduces the iron, thus preventing it from coming down with the alumina.

Heat just to boiling, add 8 c.cs. acetic acid and 15 c.cs. ammonium acetate solution and boil for 10 minutes. Allow the precipitate to settle, filter as rapidly as possible, and wash thoroughly with hot water. Ignite at a low temperature till the filter-paper has completely burned off, then at an increased temperature till constant in weight. Cool and weigh as AlPO_4 . Factor = .22187 aluminium.

16. CHROMIUM.

Through the solution containing the chromium, pass sulphur dioxide gas to saturation, thus ensuring the complete reduction of any iron present, then add slight excess of ammonia. Heat the solution to just below boiling point and digest at this temperature till the supernatant liquor has become perfectly colourless.

Filter, wash thoroughly with hot water. Ignite at a low temperature till the paper has burned away. Increase the temperature to bright redness and continue the ignition till constant in weight. Weigh as Cr_2O_3 . Factor = .68463 chromium.

17. ZINC PYROPHOSPHATE.

Cool the solution containing the zinc and add 50 c.cs. of a 10 per cent. solution of ammonium phosphate. Neutralize carefully with ammonia, using litmus as an indicator, and add 2 drops in excess. Now add 1 drop of acetic acid in excess, testing with litmus to make sure the solution is acid. Digest for one hour, but do not boil. When the precipitate has become granular and settled, filter and wash with hot water, dry, and separate

from the paper. Dissolve any precipitate adhering to the paper in a little dilute nitric acid and collect in a small weighed porcelain dish. Evaporate the solution to dryness, add the dry precipitate and heat gently to a low red heat. Cool in a desiccator and weigh as zinc pyrophosphate. Factor = .4289 zinc.

18. ZINC.

If, in the solution containing the zinc, there are no other metals, heat to boiling, and add excess of sodium carbonate and boil. The zinc is thus precipitated as hydroxide and carbonate combined. Allow the precipitate to settle and wash two or three times by decantation. Transfer to a filter and wash free from alkali. Dry, ignite, and weigh the remaining zinc. If the zinc contains other metals, they must be previously separated. The zinc is precipitated as sulphide by ammonium sulphide from an ammoniacal solution, filtered, washed, dissolved in hydrochloric acid (boiling dilute). Wash the filter, and proceed with the precipitation as above. Factor = .802 zinc.

19. MANGANESE.

To the solution containing the manganese add bromine (not bromine water) until, on stirring, the solution acquires a light port wine colour. Now add excess of ammonia and boil for one minute. The manganese is thus precipitated as manganese oxide, which is filtered, washed, ignited and weighed as Mn_2O_4 . Factor = .720 manganese.

Before adding the ammonia, allow the port wine coloured solution to stand for half an hour to ensure the manganese being completely oxidized.

20. NICKEL AS OXIDE.

To the solution containing the nickel add slight excess of caustic soda solution, heat nearly to boiling, and

allow the precipitate to settle. Filter, wash three times by decantation, and then thoroughly with hot water until the washings cease to give a precipitate with barium chloride solution. Separate the precipitate from the paper and ignite the latter first, afterwards adding the precipitate.

Finish the ignition over the blowpipe.

NOTE 1.—If the solution containing the nickel also contains ammonium salts or organic salts, it is necessary to precipitate the nickel by ammonium sulphide, re-dissolving the precipitate in nitric acid and proceeding with the estimation as described above.

NOTE 2.—In igniting the precipitate care must be taken that the flame does not enter the crucible, else the result will be low, owing to the reduction of the oxide to metallic nickel. Factor = $\cdot 78194$ nickel.

21. NICKEL, DIMETHYLGLYOXIME METHOD.

To the ammoniacal solution containing the nickel is added 5 grams ammonium chloride and the solution just neutralized with hydrochloric acid, and treated with $\cdot 4$ gram dimethylglyoxime (dissolved in alcohol) for every $\cdot 1$ gram nickel supposed to be present, ammonia is added drop by drop till just ammoniacal and the solution digested just below boiling-point for half an hour. Filter through a weighed filter paper. Wash with hot water, dry at 100° C., and weigh as $C_8H_{14}O_{11}N_4Ni$. Factor = $\cdot 2031$ nickel.

22. COBALT, PHOSPHATE METHOD.

To the solution containing cobalt, add excess of a solution of ammonium phosphate, about 5 c.cs. hydrochloric acid, and boil for several minutes to ensure the P_2O_5 being in the ortho state, cool slightly, and add ammonia in small quantities at a time till the precipitate

first produced is dissolved. Stir vigorously for a minute when the cobalt will settle out in a fine purple precipitate (ammonia phosphate of cobalt). Add 10 drops of ammonia and heat on the water bath for a few minutes. When the precipitate has settled, filter, wash with cold water, ignite, and weigh as $\text{Co}_3\text{P}_2\text{O}_4$. Factor = .404 cobalt.

23. COBALT AS OXIDE.

To the solution containing the cobalt, add 20 c.cs. hydrochloric acid, and evaporate to 100 c.cs. bulk. Precipitate the cobalt by adding 30 c.cs. of a 2 per cent. solution in alcohol of nitroso-B-naphthol. Wash the precipitate with cold water containing $\frac{1}{10}$ of its bulk of hydrochloric acid, then with pure water. Ignite in a weighed capsule to intense redness, and continue igniting till constant in weight when the cobalt is obtained as Co_3O_4 . Factor = .73444 cobalt.

24. TUNGSTEN.

Evaporate the solution containing the tungsten, add 20 c.cs. hydrochloric acid and 20 c.cs. nitric, and evaporate to complete dryness. Take up again with 10 c.cs. hydrochloric acid, 100 c.cs. water, and boil thoroughly.

Allow the $\text{SiO}_2 + \text{WO}_3$ to settle, filter, wash thoroughly with hot water, and ignite in a platinum capsule.

Drench this ignited precipitate with sulphuric acid, add 10 c.cs. hydrofluoric acid, and heat till dense fumes of sulphuric acid are given off, then completely drive off sulphuric acid by heating the capsule from the top. Ignite at a high temperature and weigh as WO_3 . Factor = .7931 tungsten.

NOTE.—As this precipitate often contains Fe_2O_3 it is advisable to always test for it, and, if found, estimate and deduct the weight obtained from the total weight found.

25. VANADIUM.

To the alkaline solution containing the vanadium as sodium vanadate, add nitric acid till only slightly alkaline. Care must be taken not to make the solution acid, otherwise the nitrous acid liberated would reduce the vanadic acid. Filter off any precipitate of silicic acid and alumina which may form, and precipitate vanadium and any chromium present by adding chloride of barium and a little ammonia. Filter, wash thoroughly, and boil the precipitate with dilute sulphuric acid in not too great excess. The reddish-yellow solution is saturated with ammonia, evaporated to small bulk, and a piece of solid ammonium chloride added. Vanadate of ammonium separates as a white or yellowish crystalline powder. Filter, wash with ammonium chloride solution. Dry and ignite gradually in a weighed porcelain capsule. The vanadic acid is obtained as a red liquid when strongly heated, which solidifies to a crystalline mass on cooling. Factor = .5618 vanadium.

26. URANIUM, PATERA'S PROCESS.

The solution containing the uranium is precipitated with caustic soda, and the orange-coloured precipitate of acid uranate of soda is filtered, washed slightly, and dried. Separate the precipitate from the paper and ignite the latter first, afterwards adding the precipitate and further igniting. This ignited precipitate is transferred to a small filter-paper washed thoroughly with hot water, ignited, and weighed as $\text{NaO}_2\text{U}_2\text{O}_3$. Factor = .876 uranium.

27. TITANIUM.

Titanium is best precipitated from an acid solution, by nearly neutralizing with ammonia, adding sodium or ammonium acetate in slight excess, and boiling. The

precipitate thus obtained is easily filtered and washed. If precipitated from a sulphuric acid solution the precipitate should be covered with ammonium carbonate and ignited till constant in weight. Cool the oxide of titanium under a desiccator and weigh quickly, as it is slightly hygroscopic. Factor for Ti=·6098 titanium.

28. PHOSPHORUS, MOLYBDATE METHOD.

Neutralize the solution containing the phosphorus, if ammoniacal, with nitric acid, and add 10 c.cs. nitric acid in excess, and warm the solution, which should not be over 50 c.cs. in bulk to 80° C. Pour into this solution 50 c.cs. ammonium molybdate, shaking all the time, and allow to stand in a warm place for half an hour. Filter through a weighed Swedish filter-paper, wash with nitric acid water (1-10), and dry in the water bath till constant in weight. Weigh a sammonio-phospho-molybdate. Factor=·0163 phosphorus.

NOTE.—It is always advisable to test the filtrate from the ammonio-phospho-molybdate by adding a little more ammonium molybdate and digesting again at 80° C. for some time. If found the precipitate must be added to the original precipitate.

29. PHOSPHORUS, MAGNESIA MIXTURE METHOD.

In the ammonium molybdate process there is always the danger of molybdic acid precipitating out and being weighed as ammonio phospho molybdate, so the following combination process is recommended.

Dissolve the ammonio phospho molybdate precipitate from the paper by copious washings with ammonia water (1-5), and to this ammoniacal solution add ammonium chloride solution and slight excess of magnesium mixture*, stir well and allow to stand for at least one hour. Filter

* Magnesia mixture p. 29.

and wash with cold ammonia water (1-5), dry, separate the precipitate from the paper, and ignite the latter first, add the precipitate and finish the ignition over the blowpipe. If the precipitate is not quite white, moisten it with strong nitric acid and again ignite till constant in weight. Weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. Factor = .27928 phosphorus.

30. SULPHUR, PRECIPITATION METHOD.

To the solution containing the sulphur, add 20 c.cs. bromine water and boil.

Add 10 c.cs. of hydrochloric acid and a slight excess of barium chloride, boil and allow the fine precipitate of barium sulphate to settle. Filter through a double, fine filter-paper, wash with hot hydrochloric acid water (1-7) four times, and finally with hot water till completely free from acid. Ignite and weigh as BaSO_4 . Factor = .1373 sulphur.

31. BORON.

Evaporate the solution containing the boron to dryness, with the addition of 10 c.cs. caustic soda solution. Add 20 c.cs. water and 20 c.cs. alcohol to dissolve sodium borate and filter into a distilling flask, fitted with a two-holed rubber cork. Through one hole passes a stoppered funnel and through the other passes the attachment to the condenser. Attach the flask to a Liebig's condenser, and run in, through the funnel, acetic acid till the solution is distinctly acid, and distil. Receive the distillate in pure lime (1 gram) previously ignited in a platinum capsule till constant in weight. The capsule should have a capacity of about 70 c.c. Distil till the solution in the flask is reduced to about 15 c.c. bulk, add 5 c.c. alcohol, and distil again. Repeat this process four times. Evaporate the contents of the capsule to dryness and ignite over the blowpipe. The increase in weight is B_2O_3 . Factor for boron is .28571.

32. MAGNESIA.

To the solution in which the magnesia is to be estimated, add ammonia, ammonium chloride solution, and finally excess of sodium phosphate, stirring well.

The magnesia is thus precipitated as ammonio magnesium phosphate. Allow to stand for two hours, filter through a Swedish filter-paper and wash with ammonia water 981° Twaddell ($4\frac{1}{2}$ -1). Dry and separate the precipitate from the paper and ignite the latter first. Continue heating for 15 minutes after the precipitate is added. If the precipitate is not white, moisten with nitric acid and re-ignite. During ignition ammonia is driven off leaving $Mg_2P_2O_7$. The precipitate is often ignited over the blowpipe. Factor = 360 magnesium.

33. MOLYBDENUM, CHATARD'S METHOD.

To the pure alkaline solution of molybdic acid, add slight excess of acetate of lead and boil for a few minutes. The precipitate, which is at first milky, becomes granular. Allow the precipitate to settle and wash thoroughly with hot water. The precipitate is dried, removed as much as possible from the paper. Ignite the paper first, add the precipitate and continue the ignition till constant and weigh as PbO, MoO_3 . Factor = 26165 molybdenum.

34. MOLYBDENUM.

The solution containing the molybdate is neutralized and 20 c.cs. of a solution of mercurous nitrate added, boil, and allow the precipitate to settle for some time.

Filter and wash with a dilute solution of mercurous nitrate (4 per cent. solution).

Dry the precipitate and separate it, as well as possible, from the paper, and add it to a porcelain crucible containing ignited oxide of lead which has been previously

weighed. Mix thoroughly with a nickel wire. Ignite the paper carefully, add the ash to the crucible and ignite till constant in weight. The increase in weight gives the amount of trioxide of molybdenum, MoO_3 . Factor = .6670 molybdenum.

35. CADMIUM AS SULPHIDE.

Through the solution containing the cadmium, which must be slightly acidified with hydrochloric acid, pass sulphuretted hydrogen gas to saturation. Filter through a weighed filter-paper and test the filtrate, by again passing the gas. If no further precipitation occurs, wash the precipitate, first with water acidified slightly with hydrochloric acid mixed with sulphuretted hydrogen water, and then with cold water. Dry the precipitate in the water bath and wash four times with carbon bisulphide, which removes any free sulphur inadvertently precipitated.

Dry in the water bath till constant in weight and weigh as cadmium sulphide. Factor = .7778 gram cadmium.

36. CADMIUM AS OXIDE.

To the solution containing the cadmium, add potassium carbonate till the cadmium is completely precipitated. Heat to 60°C . and allow to settle for some time. Filter through a Swedish filter-paper and wash thoroughly. Dry the filter-paper and contents in the water bath, remove the precipitate, as perfectly as possible, from the paper, drench the paper with solution of ammonium nitrate, dry, and ignite. Add the precipitate to the capsule and ignite till constant in weight.

NOTE 1.—It is difficult to remove the last traces of carbonic acid, so repeated ignitions may be found necessary.

NOTE 2.—Avoid the action of reducing gases, therefore do not allow the flame to play inside the capsule. Factor = .875 gram cadmium.

37. TUNGSTEN, CINCHONINE METHOD.

To the hydrochloric acid solution of tungsten, add a solution of cinchonine, made by dissolving 25 grams cinchonine in 200 c.cs. hydrochloric acid water (1-1). Add a slight excess of this solution which precipitates tungsten almost immediately. Allow the precipitate to settle, filter, wash thoroughly, ignite, and weigh as WO_3 .

NOTE.—If molybdenum is present it must first be separated, as cinchonine precipitates molybdenum partially after standing a considerable time. Factor = .7931 tungsten.

38. CALCIUM.

To the solution containing the calcium, add ammonia and ammonium chloride till strongly alkaline, boil, and add a solution of ammonium oxalate.

The calcium is thus precipitated as calcium oxalate. Allow the precipitate to settle for one hour, filter through a Swedish filter-paper, wash with hot water, ignite, and weigh. During ignition some of the calcium oxalate is decomposed to calcium oxide, so it is necessary to drench the precipitate with a saturated solution of ammonium carbonate and dry over the blue flame of an Argand burner to ensure a homogeneous precipitate of calcium carbonate. Dry till constant in weight. An alternative method is to ignite the precipitate strongly over the foot blowpipe to convert the precipitate into calcium oxide. This method is not so satisfactory, owing to the difficulty of completely decomposing the carbonate of lime. If weighed as carbonate, Factor = .400 calcium; as oxide, Factor = .71427 calcium.

CHAPTER VI

SEPARATION METHODS

39. OXIDES OF IRON AND ALUMINA.

DISSOLVE the oxides of iron and alumina in dilute hydrochloric acid (1-2), add 5 c.cs. of nitric acid and boil for a few minutes. Add caustic soda solution till all the iron has completely precipitated, using as little excess as possible, boil, allow to settle, filter off the iron, and wash thoroughly. The filtrate contains all the alumina. The filtrate is made slightly acid with hydrochloric acid, 5 c.cs. of nitric acid are added and the solution boiled. Proceed as described in PAR. 14. Alumina Al_2O_3 .

The iron precipitate is dissolved by passing boiling dilute hydrochloric acid (1-4) through the paper, wash the paper thoroughly free from all traces of yellow colour, and to the filtrate and washings add 10 c.cs. nitric acid and boil. Proceed as described in PAR. 12. Iron oxide, Fe_2O_3 , or by the volumetric method described subsequently (PAR. 90).

40. IRON AND MANGANESE.

The solution containing the iron and manganese is boiled with 10 c.cs. of nitric acid and the iron separated by the ammonium acetate method (PAR. 13). The filtrate is now cooled, bromine (not bromine water) is added till the solution acquires a light port wine colour, and the estimation of manganese proceeded with as described in PAR. 19.

41. SEPARATION OF ALUMINA FROM OXIDES OF ZINC.

Sometimes the oxide of zinc precipitates contain traces of alumina, which may be separated and estimated thus. Dissolve the oxide of zinc precipitate containing the alumina in 10 c.cs. hydrochloric acid, dilute to 200 c.cs. with water, add 30 c.cs. ammonium acetate solution and 5 c.cs. acetic acid. Pass H_2S through the solution till the zinc is precipitated. Filter and wash. Add some sodium phosphate solution to the filtrate, neutralize with ammonia, and collect the phosphate of alumina precipitate, wash, and proceed as described in PAR. 15. Dissolve the sulphide of zinc from the filter-paper by means of sulphuric acid water (1-4), wash the paper thoroughly and proceed with the estimation of zinc as described in PAR. 18, or preferably by the volumetric method described in PAR. 82.

42. SEPARATION OF NICKEL AND COBALT.

Mix the solution containing the nickel and cobalt with excess of ammonium phosphate, add 5 c.cs. hydrochloric acid and boil for several minutes to make sure all the P_2O_5 is in the ortho state. Remove the beaker from the source of heat, and, while nearly boiling, add ammonia in small quantities at a time till the precipitate first produced is dissolved. Stir vigorously for some time when the cobalt will separate out as a fine purple precipitate (ammonia phosphate of cobalt), add 10 drops of ammonia, and heat on the top of the water bath till the precipitate has settled. Filter, wash with cold water, ignite, and weigh as $Co_2P_2O_4$. Factor = 404.

Boil the filtrate till the nickel begins to precipitate out. The precipitate will be reddish if any cobalt is still present, which must be separated as before. Saturate

the ammoniacal filtrate with H_2S which precipitates nickel. Filter off nickel sulphide, dissolve the precipitate in aqua regia, and estimate nickel as described in PARS. 20 and 21.

43. NICKEL AND ZINC.

To the ammoniacal solution containing the nickel and zinc add 20 c.cs. ammonium chloride solution and exactly neutralize with hydrochloric acid or leave only very slightly alkaline. Now add a solution of dimethylglyoxime in alcohol (about .4 gram dimethyl for every .1 gram nickel supposed to be present), add a few drops of ammonia and digest for half an hour just below boiling point. Collect the precipitate on a weighed filter-paper, wash with hot water, dry at $100^\circ C.$ and weigh as $C_8H_{14}O_{11}N_4Ni$. Factor = .2031 nickel.

The filtrate is acidified with an excess of hydrochloric acid, boiled to decompose the excess of dimethylglyoxime, and 10 grams of sodium phosphate are added. The solution is now exactly neutralized with ammonia and digested on the hot plate just below boiling-point till the precipitate has granulated. This precipitate is collected on a filter-paper, washed with hot water, ignited, and weighed as zinc pyrophosphate. Factor = .4289 zinc.

44. NICKEL AND COBALT. MODIFICATION OF ROSE'S METHOD.

To the dilute solution containing the nickel and cobalt, add 10 c.cs. hydrochloric acid, boil, and add slight excess of barium carbonate. Cool and add bromine, when, on standing for 10 minutes, the cobalt will separate out completely as cobalt sesquioxide Co_2O_3 . Factor = .5514 cobalt.

The filtrate is made alkaline with ammonia, boiled,

and the nickel precipitated with dimethylglyoxime, as described in PAR. 21, or as oxide as described in PAR. 20.

45. TIN AND ANTIMONY OXIDES.

To the mixed oxides of tin and antimony, add hydrochloric acid and digest on the hot plate till the oxides have dissolved. A crystal or two of potassium chlorate, added carefully occasionally, will assist solution. Add 5 grams of freshly precipitated copper, made by immersing strips of aluminium or zinc in a solution of copper sulphate, slightly acidified with sulphuric acid. Wash the copper thus obtained with hydrochloric acid and then free from acid with hot water. Digest the solution, to which has been added the spongy copper, for half an hour on the hot plate, filter off the precipitated antimony and copper, preserving the filtrate for tin. Dissolve the spongy precipitate in nitric acid, add 5 drops of mercuric chloride, and finish the estimation of antimony as described in PAR. 8.

Treat the filtrate from the antimony exactly as described in PAR. 5 for the estimation of tin.

46. TIN AND ANTIMONY IN SOLUTION.

To the solution containing the tin and antimony, add 10 c.cs. hydrochloric acid, if not already present, and 20 grams oxalic acid, dilute to 300 c.cs., boil, and pass a rapid stream of H_2S through the hot solution. When the antimony is completely precipitated, filter at once, and proceed with the estimation of antimony, as in PAR. 7.

In the filtrate from the antimony, the oxalic acid must be completely destroyed before precipitating the tin. Add hydrochloric acid in excess and then, carefully, potassium permanganate until a small precipitate of

MnO_2 remains which does not dissolve on boiling. Redissolve this precipitate of MnO_2 by adding a few drops of ferrous sulphate solution, and precipitate the tin by passing H_2S gas. Proceed with this precipitate as described in PAR. 5.

47. ANTIMONY AND ARSENIC.

The mixture of the sulphides and sulphur, obtained in the usual way by the addition of acid to the ammonium sulphide solution, is extracted with a cold 5 per cent. solution of sodium sulphide. The metallic sulphides dissolve readily, leaving the sulphur in suspension. Filter off the sulphur and wash thoroughly. To the filtrate, add about twice as much 10 per cent. caustic soda solution as was added of sodium sulphide, then 20 c.cs. of hydrogen peroxide, and heat to boiling. The antimony separates out in glistening crystals on the addition of $\frac{1}{6}$ of the bulk of solution of methylated spirits. Filter off this precipitate and wash with water containing $\frac{1}{8}$ of its bulk of methylated spirits. Ignite at a dull red heat and weigh as NaSbO_3 . Factor = '62822 antimony.

From the filtrate, boil off methylated spirits and add ammonia and magnesia mixture. Complete the estimation of arsenic as in PAR. 9.

48. TUNGSTEN AND MOLYBDENUM.

Heat the alkaline solution containing the tungsten and molybdenum to boiling, and add a few c.cs. of a solution of 50 grams stannous chloride in 200 c.cs. hydrochloric acid. The amount must be regulated approximately to 20 c.cs. per .15 gram of tungsten trioxide. After the solution has boiled for some minutes, the blue precipitate of W_2O_5 is allowed to settle, filtered, and washed with a

5 per cent. solution of hydrochloric acid water, ignited in a weighed porcelain crucible, cooled in a desiccator, and weighed as tungsten trioxide. Factor= $\cdot 7931$ tungsten.

To the filtrate from the tungsten, add 5-10 grams zinc which has passed through a 20-mesh sieve, which precipitates tin in the metallic form, wash this precipitate thoroughly. The filtrate contains all the molybdenum present. Neutralize the solution carefully with nitric acid, add a slight excess of a solution of lead acetate, which precipitates molybdenum, boil, allow the precipitate to settle, filter, wash with hot water, dry, separate the precipitate from the paper, and ignite the latter first, afterwards adding the precipitate and igniting till constant in weight. Factor= $\cdot 26165$ molybdenum.

49. SEPARATION OF VANADIUM AND CHROMIUM.

To the alkaline solution of vanadium and chromium, add nitric acid, carefully, till only very slightly alkaline, filter off any precipitate and add solution of barium chloride and ammonia in slight excess, which precipitates chromium and vanadium. The precipitate is boiled with a slight excess of sulphuric acid, and the precipitated barium sulphate filtered off and washed with hot water. To the reddish-yellow filtrate, add ammonia and evaporate to small bulk.

On adding a piece of solid ammonium chloride, vanadate of ammonium separates out. Filter, wash with ammonium chloride water (5 per cent.). Ignite and weigh as vanadic oxide. Factor= $\cdot 5614$ vanadium.

To the filtrate, add sulphurous acid which will precipitate chromium as hydrated oxide of chromium. Filter off this precipitate, wash with hot water, ignite, and weigh as Cr_2O_3 . Factor= $\cdot 686$ chromium.

50. SEPARATION OF NICKEL AND COBALT.

The mixed nickel and cobalt sulphides are dissolved in nitric acid water (1-3), and caustic soda added, carefully, till the precipitate just remains permanent after stirring some time. Add acetic acid to dissolve the precipitate and a strong solution of potassium nitrite, which precipitates cobalt as the double nitrite of cobalt and potassium. Allow to stand for some time and filter, wash with water, then with alcohol, dry, and weigh. The filtrate contains the nickel. Of the weighed double salt take an aliquot part, transfer to a porcelain crucible, and heat cautiously with sulphuric acid. Expel the excess of acid and ignite at a low temperature and weigh as $3K_2SO_4 \cdot CoSO_4$. Factor = .1417 gram cobalt.

Nickel is precipitated in the filtrate by the dimethylglyoxime method, as described in PAR. 21.

51. BISMUTH AND LEAD CHROMATE METHOD.

Neutralize the solution carefully, add 1 gram ammonium acetate and 2 c.cs. glacial acetic acid. Precipitate lead and bismuth by adding solution of potassium bichromate.

Add slight excess of caustic soda solution which dissolves lead chromate, and filter off bismuth chromate through a weighed filter paper, wash completely free from alkali, dry till constant, and weigh as $BiO_3 \cdot (Cr_2O_3)_2$. Factor = .62561 gram bismuth.

Acidify the filtrate with acetic acid, which reprecipitates lead chromate. Filter through a weighed filter paper, wash thoroughly, dry till constant, and weigh as $PbOCrO_3$. Factor = .64055 gram lead.

52. IRON AND NICKEL.

To the solution containing iron and nickel, add 5 c.cs. nitric acid, and boil thoroughly. Now add 20 c.cs. of

ammonium chloride and excess of ammonia to precipitate iron. Filter and wash thoroughly with hot water, redissolve the precipitate in hydrochloric acid, add 5 c.cs. nitric acid, boil, and reprecipitate the iron by means of ammonium chloride and ammonia as before. Filter, wash thoroughly, and add this filtrate to the first filtrate. Ignite and weigh the precipitate as Fe_2O_3 .

To the filtrate, add slight excess of ammonium sulphide and neutralize with acetic acid, which precipitates the nickel as sulphide. Neutralization with acetic acid is necessary, otherwise the precipitation is incomplete, owing to the slight solubility of nickel sulphide in ammonia. Filter off this precipitate, redissolve by pouring hot dilute nitric acid (1-4) through the paper, and precipitate nickel as described in PAR. 20 or PAR. 21.

CHAPTER VII

VOLUMETRIC ESTIMATIONS

WHENEVER possible volumetric processes should be adopted, as they are usually speedier and less liable to error than gravimetric estimations.

The following list of standard solutions, with the indicators used, approximate factors, and hints on storing and standardizing, will cover all the volumetric processes given in this volume.

STANDARDS, ETC.

53. N/10 IODINE.

Dissolve 12.8 grams of resublimed iodine in distilled water, using about 20 grams potassium iodide as a catalyst, small quantities at a time, till the iodide has completely dissolved. Dilute to 1 litre with distilled water. The N/10 iodine should be stored in a brown glass bottle, tightly stoppered, and stored in a cool place, away from direct sunlight. Shake well before using, as drops of moisture condense on the walls of the bottle, which, if not thoroughly admixed, render the solution stronger, consequently giving low results. If the solution is not in general use, it must be standardized frequently, as it loses strength on keeping.

Solution used for the volumetric estimation of tin.
Factor = .006 gram tin approximately.

Indicator: Starch solution is used as an indicator.

It must be freshly prepared, or not more than two days old, otherwise the end reaction becomes less sharp.

It is conveniently made by making 1 gram of powdered starch into a cream with cold water, and adding to 500 c.cs. of boiling distilled water, boiling for one minute, allowing to settle, and decanting the clear supernatant liquor into a tightly stoppered bottle.

Reactions : Blue with iodine. Blue colour destroyed with sodium hyposulphite.

54. STANDARD METHYLENE BLUE.

1 gram of methylene blue dissolved in 1 litre of water.

Indicator: Internal colour change. Used for the estimation of tin.

55. N/10 SODIUM HYPOSULPHITE.

Dissolve 25 grams of commercial sodium hyposulphite in 1 litre of distilled water. Store in a brown glass stoppered bottle in a cool place. The addition of sodium chloride, as is generally supposed, does not affect the storing properties beneficially. If the stock solution is stored in bottles of about 500 c.cs. capacity completely filled and sealed till required for use, the solution will keep for at least six months.

Indicator: (1) Starch solution (PAR. 53).

(2) 10 per cent. sodium salicylate solution
for iron, or

(3) Methylene blue.

Methylene blue .05 gram per litre will be found to give accurate results in iodometric titrations. It may be introduced at the beginning of the titration, and the colour change is unaffected by the presence of neutral salts, acetic, nitric, and sulphuric acids. It is particularly

useful in the estimation of antimony, as the end reaction is very decided.

Reaction : Iodine decolorizes.

Blue colour produced with sodium hyposulphite.

Factors : 1 c.c.

=·0061 gram antimony approximately.

=·0063 „ copper „

=·01035 „ lead „

=·0059 „ cobalt „

=·0056 „ iron „

56. N/10 AMMONIUM MOLYBDATE.

Dissolve 9 grams ammonium molybdate in 1 litre of distilled water.

Store in a stoppered bottle in a cool place. This solution keeps very well unchanged.

Indicator : 2 gram tannic acid dissolved in 100 c.cs. distilled water, freshly prepared, or not more than a few hours old.

Reaction : Spotted on a white plate, canary colour produced.

Used for the estimation of lead. Factor : 1 c.c. =·01 gram lead approximately.

57. N/10 POTASSIUM BICHROMATE.

Dissolve 4·92 grams of pure dry recrystallized bichromate of potash in 1 litre of distilled water. Stored in a stoppered bottle in a cool place, the solution keeps well.

Indicator : A small crystal of potassium ferricyanide dissolved in 20 c.cs. of distilled water, prepared immediately before use.

Reaction : When all the ferrous salt has been oxidized the blue colour is no longer produced.

Used externally on a white porcelain plate.

Used in the estimation of iron and manganese.

Factors: 1 c.c. = .0056 gram iron approximately.

= .00275 „ manganese approximately.

58. N/10 POTASSIUM FERROCYANIDE.

Dissolve 14.06 grams potassium ferrocyanide in 1 litre of distilled water. Stored in a tightly stoppered bottle in a cool place, away from direct sunlight, the solution keeps fairly well.

Indicator: Glacial acetic acid, used externally on a white porcelain plate. A blue colour produced.

Used for the estimation of zinc. Factor: 1 c.c. = .0044 gram zinc approximately.

59. STANDARD POTASSIUM FERROCYANIDE.

Dissolve 21.63 grams of potassium ferrocyanide and 7 grams of sodium sulphite in 1 litre of distilled water.

Stored in a tightly stoppered bottle in a cool place, away from direct sunlight, this solution keeps fairly well.

Indicators: All used externally spotted on a white porcelain plate.

(1) Uranium nitrate, 1 gram dissolved in 20 c.cs. distilled water.

End reaction: Red-brown coloration.

(2) Uranium acetate, 1 gram dissolved in 20 c.cs. distilled water.

End reaction: Red-brown coloration.

(3) Ammonium molybdate, 1 gram dissolved in 100 c.cs. distilled water.

End reaction: Red-brown coloration.

Factors: 1 c.c. = .0062 gram zinc approximately.

= .015 „ lead „

60. SODIUM SULPHIDE.

Prepare a solution of sodium sulphide by passing hydrogen sulphide gas through a solution of caustic soda of 1.05 specific gravity, until it gives no precipitate with magnesium sulphate solution, showing the reaction to be complete. This solution is usually diluted so that 1 c.c. will equal .005 gram of zinc.

Indicators: All used externally, spotted on a white porcelain plate.

(1) Cobalt nitrate, .2 gram dissolved in 20 c.cs. distilled water.

End reaction: Brownish-black coloration.

(2) Cobalt chloride, .2 gram dissolved in 20 c.cs. distilled water.

End reaction: Brownish-black coloration.

(3) Tartar emetic, saturated solution.

End reaction: Brownish-black coloration.

(4) Lead acetate, .2 gram dissolved in 20 c.cs. distilled water.

End reaction: Brownish-black coloration.

(5) Sodium nitroprusside, .2 gram dissolved in 30 c.cs. distilled water.

End reaction: Fine purple colour.

Used in the estimation of zinc. Factor: 1 c.c. = .005 gram zinc.

61. N/1 SULPHURIC ACID.

Dilute 49.043 grams sulphuric acid to 1 litre with distilled water, cool, and standardize against ignited sodium carbonate.

62. N/1 CAUSTIC POTASH.

Make up this solution of such a strength that 100 c.cs. will neutralize 32.6 c.cs. of N/1 sulphuric acid (PAR. 61). It must be freed from carbonate by barium hydrate.

Indicator: Internal, phenolphthalein.

Dissolve 2 gram phenolphthalein in 20 c.cs. alcohol and dilute to 250 c.cs. with water and methylated spirits (1-1).

Reaction: Pink titrated to colourless, used in the estimation of phosphorus.

63. STANDARD URANIUM ACETATE.

Dissolve 29 grams uranium acetate in water, add 25 c.cs. glacial acetic acid, and dilute to 1 litre with distilled water.

Solvent solution: 100 grams sodium acetate dissolved in distilled water, 100 c.cs. acetic acid added, and diluted to 1 litre with distilled water.

Indicator: 2 gram potassium ferrocyanide dissolved in 100 c.cs. distilled water.

Used externally spotted on a white porcelain plate.

End reaction: pale red-brown coloration.

Used for the estimation of magnesium.

Factor: 1 c.c. = 0.0017 gram magnesium.

64. STANDARD ARSENIOUS ACID.

Dissolve 1 gram arsenious acid and 2 grams sodium bicarbonate in distilled water, if necessary by means of heat, cool, and dilute to 1 litre with distilled water.

Indicator: Internal colour change.

Used for the estimation of manganese. Factor: 1 c.c. = 0.005 gram manganese.

65. STANDARD STANNOUS CHLORIDE.

Dissolve 15.45 grams of stannous chloride in 200 c.cs. hydrochloric acid and dilute to 1 litre with distilled water.

Indicator: Methylene blue (PAR. 55).

Store in a cool place away from direct sunlight. This

solution must be frequently standardized, as it does not keep well.

Used in the estimation of ferric iron.

Factor 1 c.c. = .005 gram iron.

66. POTASSIUM CYANIDE.

Dissolve 50 grams potassium cyanide in 1 litre distilled water. This solution keeps well if stored in a tightly stoppered bottle, in a cool place, away from direct sunlight.

Indicator: Internal colour change.

Used for the estimation of copper.

Factor 1 c.c. = .00635 gram copper approximately.

67. STANDARD IODINE.

Dissolve 1.69 grams resublimed iodine in distilled water, using 5 grams potassium iodine as a catalyst, a little at a time till dissolved. Dilute to 1 litre with distilled water.

Re storing, the same remarks apply as in PAR. 53, N/10 iodine.

Indicators: (1) starch solution (PAR. 53).

(2) or methylene blue (PAR. 55).

Used in the estimation of arsenic.

Factor 1 c.c. = .0005 gram arsenic.

68. STANDARD SILVER NITRATE AND POTASSIUM CYANIDE.

Dissolve 12 grams potassium cyanide in distilled water and 1 gram silver nitrate in distilled water, mix and dilute to 1 litre with distilled water.

Indicator: Dissolve 50 grams citric acid in distilled water and add sodium carbonate carefully till the solution is neutral (about 38 grams required), add 10 grams of

potassium iodide dissolved in distilled water and dilute to 500 c.cs. This solution should be neutral or very slightly alkaline.

Standard solution should be stored in a brown bottle, in a cool place, away from direct sunlight, and should be frequently standardized.

Used for the estimation of nickel.

Factor 1 c.c. = .0025 gram nickel.

69. STANDARD SODIUM PHOSPHATE.

Dissolve 29.835 grams of sodium hydric phosphate in 1 litre distilled water. Store in a stoppered bottle in a cool place. Standardize this solution against a uranium salt with a known content of uranium.

Indicator: Used externally on a white porcelain plate. Potassium ferrocyanide (PAR. 63).

Used in the estimation of uranium.

Factor 1 c.c. = .02 gram uranium approximately.

70. N/10 POTASSIUM PERMANGANATE.

Dissolve 3.16 grams of potassium permanganate in 1 litre of distilled water. Store in a brown glass-stoppered bottle, in a cool place, away from direct sunlight.

Indicator: Internal colour change.

Standardize: Weigh out 1 gram pure oxalic acid, dissolve in distilled water, dilute to 500 c.cs. and pipette off 100 c.cs. Add 10 c.cs. concentrated sulphuric acid, heat to 60° C., and titrate with the standard until a faint pink coloration persists, on constant stirring, .2 gram divided by the number of c.cs. consumed, gives the value of 1 c.c. in terms of oxalic acid.

Used in the estimation of bismuth, cadmium, oxalic acid, ferrous sulphate, ferrous ammonium sulphate, titanium, vanadium.

Factors 1 c.c. =	0104	gram bismuth approximately.
=	0086	„ cadmium „
=	0045	„ oxalic acid „
=	0278	„ ferrous sulphate approximately.
=	03921	„ ferrous ammonium sulphate approximately.
=	01191	„ uranium approximately.
=	00481	„ titanium „
=	0051	„ vanadium „

It is always advisable to standardize the solution directly against cadmium salts containing a known quantity of cadmium precipitated as oxalate as in the method described under the heading Cadmium (PAR. 98).

71. STANDARD AMMONIUM SULPHO-CYANIDE.

Dissolve 7.8 grams ammonium sulphocyanide in 1 litre of distilled water.

Indicator: 5 grams iron ammonia alum dissolved in 100 c.cs. distilled water.

End reaction: red coloration.

Standardize against silver nitrate (PAR. 104), and arsenious acid (PAR. 109).

Factor 1 c.c. = 01 gram silver approximately.

= 0025 gram arsenic „

72. STANDARD SULPHURIC ACID.

Dilute 8.3 c.cs. of sulphuric acid 1.84 specific gravity to 1 litre with distilled water.

Standard Caustic Potash: Dissolve 16.4 grams caustic potash in 1 litre distilled water. 1 c.c. should equal 1 c.c. of the above standard sulphuric acid, but should be tested and carefully adjusted.

Indicator: Phenolphthalein (PAR. 62).

Used for the estimation of aluminium.

Factor 1 c.c. = .005 gram alumina (Al_2O_3).

= .00265 gram aluminium.

Standardizing: Dissolve 1 gram of potash alum in 100 c.cs. of distilled water, add 2 grams sodium peroxide, and boil. Add 5 c.cs. phenolphthalein and neutralize exactly, add 20 c.cs. normal sulphuric acid, boil, add 5 c.cs. phenolphthalein, and titrate with standard caustic potash. .1086 gram divided by the c.cs. of sulphuric acid consumed will give the factor.

73. STANDARD LEAD ACETATE.

Dissolve 19.5 grams of lead acetate in distilled water, slightly acidify with acetic acid, and dilute to 1 litre with distilled water.

Indicator: Tannic acid (PAR. 56).

Used externally spotted on a white porcelain plate.

Standardize this solution against ammonium molybdate containing a known quantity of molybdenum.

Used for the estimation of molybdenum.

Factor 1 c.c. = .005 gram molybdenum approximately.

74. STANDARD BARIUM CHLORIDE.

Dissolve 36.25 grams crystallized barium chloride in 1 litre of distilled water.

Indicator: 1 gram potassium chromate dissolved in 100 c.cs. distilled water.

Used externally spotted on a white porcelain plate.

Standardize this solution against any soluble sulphate of known composition.

Factor 1 c.c. = .005 gram sulphur.

75. N/10 CAUSTIC SODA.

Dissolve 40 grams caustic soda in 1 litre of distilled water.

Indicator: Phenolphthalein (PAR. 62).

Standardize this solution against boric acid by the method described in PAR. 112.

MANIPULATION.

76. TIN.

Standard: N/10 iodine solution (PAR. 53).

Indicator: (Internal) starch solution (PAR. 53).

Standardizing: 2 gram chemically pure tin is carefully weighed out and transferred to a conical flask, fitted with an exit tube. Add 30 c.cs. hydrochloric acid and digest on a hot plate, till completely dissolved. Place in the flask a stout iron nail or steel drillings and digest again for a further 20 minutes, to ensure the tin being completely reduced to the stannous state, dilute to 250 c.cs. with cold water, filter rapidly into a flask from which the air has been expelled by passing carbon dioxide gas, wash with cold water, add starch solution and titrate with the iodine solution till 1 drop produces a permanent blue colour.

2 gram used divided by the c.cs. consumed gives the value of 1 c.c.

Factor = approximately 0060 gram tin.

77. TIN.

Standard: Methylene blue (PAR. 54).

Indicator: (Internal) colour change.

Weigh out accurately 2 gram pure tin and place in a flask fitted with an exit tube, add 30 c.cs. hydrochloric acid and digest on the hot plate till completely dissolved. Add an iron nail or steel drillings to the solution and digest for a further 20 minutes, dilute to 100 c.cs. with cold water, filter rapidly, add 30 c.cs. hydrochloric acid, dilute to

300 c.cs. bulk and titrate with the standard till a permanent blue colour is produced.

'2 gram divided by the number of c.cs. consumed gives the factor for 1 c.c. standard solution.

Factor 1 c.c. = '002 gram tin approximately.

78. ANTIMONY.

Standard Solution: N/10 sodium hyposulphite (PAR. 55).

Indicator: (Internal) starch solution (PAR. 53); or methylene blue (PAR. 55).

Weigh out accurately '2 gram pure antimony and treat on a hot plate with 20 c.cs. nitric acid water (1-2) till completely oxidized. Absolutely no black or grey specks should remain. Add 5 drops mercuric chloride and 50 c.cs. water, boil up and allow to settle.

Filter through a very fine filter-paper and wash thoroughly. (Black papers are preferable.) Wash from the paper with as little hot water as possible, into the original beaker; add 20 c.cs. hydrochloric acid and dissolve by digesting on the hot plate. Add 10 c.cs. hydrogen peroxide, and boil for half an hour. Cool to the room temperature, add about 1 gram potassium iodide, and titrate the liberated iodine with the standard solution, using starch solution or methylene blue as an indicator. In titrating the iodine it is better to add the standard solution till the brown colour has faded to a lemon yellow, before adding the indicator. Continue adding the standard till the blue colour produced on the addition of the starch solution is just destroyed.

Methylene blue is preferable as an indicator in this estimation as the end reaction is more sensitive.

Factor is found by dividing '2 gram (quantity used) by the number of c.cs. consumed.

Factor 1 c.c. = '0061 gram antimony.

79. LEAD, AMMONIUM MOLYBDATE METHOD.

Standard: N/10 ammonium molybdate (PAR. 56).

Indicator: (External) tannic acid solution (PAR. 56).

Weigh out accurately .5 gram pure dry lead sulphate into a beaker and dissolve by adding a solution of ammonium acetate to which has been added a few drops of acetic acid. A stock solution of 1.036 specific gravity should be kept in stock. One part of lead is soluble in 47 parts of this solution. When the lead sulphate has completely dissolved, dilute to about 200 c.cs. and reserve 20 c.cs. Titrate the bulk of the solution (boiling) with the N/10 molybdate solution, boiling between each addition till 1 drop applied to a spot of the indicator on a white porcelain plate, produces a distinct canary colour. Add the reserved 20 c.cs. to the bulk and complete the estimation carefully, as .5 gram lead sulphate contains .34147 gram lead, divide that figure by the number of c.cs. consumed to find the value of 1 c.c.

Factor 1 c.c. approximately = .01 gram lead.

NOTE.—Some chemists prepare a solution of lead acetate, 10 c.cs. of which equal 10 c.cs. ammonium molybdate, to be used in case of over-titration. This solution is used in case of over-titration by adding 5 c.cs. and finishing the estimation carefully, deducting the 5 c.cs. from the total number of c.cs. consumed and calculating as usual.

80. LEAD CHROMATE.

Standard: N/10 sodium hyposulphite (PAR. 55).

Indicator: Starch or methylene blue (PAR. 53 or 55).

.3 gram pure lead foil or .5 gram pure lead sulphate are used for standardizing the hyposulphite solution.

The lead foil is dissolved in nitric acid, and lead sulphate produced as described in PAR. 1.

The lead sulphate is dissolved in boiling solution of sodium acetate, and the solution neutralized with caustic soda, using phenolphthalein as an indicator, the pink colour being then discharged with acetic acid. 10 c.cs. of 10 per cent. potassium bichromate are then added, and the liquid boiled for a few minutes. The lead chromate is filtered and washed with hot sodium acetate solution (50 c.cs. cold saturated solution per litre), and the precipitate dissolved in cold dilute HCl (1-2).

The chromic acid liberated represents the lead, and is estimated by adding 2 c.cs. 50 per cent. potassium iodide solution, and titrating the liberated iodine with the standard, using starch solution as an indicator. The value of 1 c.c. of the standard is calculated as usual.

Factor 1 c.c. = .01035 lead approximately.

81. LEAD, AMMONIACAL SOLUTION.

Standard: Potassium ferrocyanide (PAR. 59).

Indicator: (External) uranium acetate (PAR. 59)

Weigh out accurately .5 gram lead sulphate (pure, dry) and dissolve in ammonium acetate solution (PAGE 29). Make slightly ammoniacal with ammonia and run in the standard, from a burette, till a drop of the solution, added to a drop of the indicator spotted on a white porcelain plate, just produces a reddish-brown colour. In this estimation the reserving of a portion of the solution, as recommended under the estimation of lead (molybdate method) (PAR. 79), is also advisable.

The factor for 1 c.c. standard is found by dividing .34147 by the number of c.cs. consumed.

Factor 1 c.c. = .015 lead approximately.

82. ZINC (AMMONIACAL).

Standard: Potassium ferrocyanide (PAR. 58).

Indicator: (External) glacial acetic acid (PAR. 58).

Weigh out .2 gram pure freshly ignited zinc oxide, dissolve in sulphuric acid water (1-4), dilute to 150 c.cs. with water, add about .5 gram sodium chloride, a few drops of saturated solution of ferric chloride and 1 gram sodium bitartrate. Boil and carefully add a slight excess of ammonia, and reserve 20 c.cs. of this solution as described under Lead (Molybdate Method) (PAR. 79). Titrate the bulk of this solution with the standard, from a burette, till a drop added to a drop of the indicator, spotted on a white poreclain plate, produces a distinct blue coloration. Add the 20 c.cs. of reserved solution and finish the estimation carefully. The solution should be titrated while boiling, and should be just alkaline.

.1606 gram zinc (the zinc content of .2 gram zinc oxide) divided by the number of c.cs. consumed, gives the factor for 1 c.c. of the standard.

Factor 1 c.c. approximately = .0044 gram zinc.

83. ZINC (ACID).

Standard: Potassium ferrocyanide (PAR. 59).

Indicator: (External) uranium nitrate, uranium acetate, or ammonium molybdate (PAR. 59).

Weigh out carefully .2 gram chemically pure zinc or .2 gram freshly ignited zinc oxide, dissolve in 30 c.cs. dilute hydrochloric acid (1-3), add 7 grams ammonium chloride, and dilute to 200 c.cs. bulk with boiling water. Titrate the boiling solution with the standard, from a burette, till a drop of the solution, added to a drop of the indicator spotted on a porcelain plate, just produces a reddish-brown coloration. Reserve 20 c.cs. of this solution as described in PAR. 79.

The value of 1 c.c. is found by dividing .2 if pure zinc was used, or .1606 if zinc oxide, by the number of c.c.s. consumed.

1 c.c. = .0062 zinc approximately.

84. ZINC.

Standard: Sodium sulphide (PAR. 60).

Indicator: (External) cobalt nitrate, lead acetate, cobalt chloride, tartar emetic, or sodium nitroprusside (PAR. 60).

.2 gram pure zinc, or .2 gram of freshly ignited zinc oxide, is dissolved in 20 c.cs. hydrochloric acid, diluted to 150 c.cs. with water and neutralized with ammonia. Add 1 gram sodium chloride and 10 c.cs. ammonia, and cool.

Add the standard solution, from a burette, till a drop of the solution, added to a drop of the indicator spotted on a white porcelain plate, just produces the end reaction desired. If cobalt nitrate indicator, a black colour will appear; if tartar emetic or sodium nitroprusside is used, a very sharp end reaction is obtained. The value of 1 c.c. standard is found by dividing .2 gram zinc, or .1606 if zinc oxide were used, by the number of c.cs. consumed.

In titrating this solution reserve about 20 c.cs., as described under the heading Lead (Molybdate Method) (PAR. 79).

85. COPPER.

Sodium hyposulphite method (PAR. 55).

Indicator: (Internal) starch solution (PAR. 53); or methylene blue (PAR. 55).

Weigh out carefully .2 gram pure copper foil, dissolve in a few drops of nitric acid, and heat on a hot plate till the brown nitrous fumes are completely driven off. Dilute with 20 c.cs. water and add a slight excess of

ammonia. Boil thoroughly, and add glacial acetic acid till the solution is slightly acid, indicated by the complete change of colour from deep blue to greenish blue. Dilute to 60 c.cs. and cool to the room temperature. Add 1 gram potassium iodide, and titrate the liberated iodine with the standard, till the brown colour fades to pale yellow. Add the indicator and finish the titration, till a drop of the standard produces no further change in colour. Divide .2 gram by the number of c.cs. consumed, to find the value of 1 c.c.

Factor approximately = .0065.

86. COPPER.

Standard : Potassium cyanide (PAR. 66).

Indicator : (Internal) colour change.

Dissolve .5 gram pure copper foil in 10 c.cs. nitric acid and heat till the brown nitrous fumes are driven off, add 20 c.cs. water, and boil. Cool, dilute to 250 c.cs. and pipette off 50 c.cs. Add ammonia carefully, till the solution is just neutralized, then add 10 c.cs. ammonia in excess, which dissolves any precipitate, and carefully titrate with the standard, till the blue colour just disappears. The mixture should be stirred thoroughly, and towards the end of the reaction should be allowed to stand for 1 minute between each addition.

Precautions.—The volume of the solution, in which the copper is to be estimated, should be as nearly as possible the same as in the blank experiment.

It is preferable to have as nearly as possible the same amount of copper in each case. If the quantity of copper present is appreciably higher, dilute the solution to 200 c.cs. and take an aliquot part, approximately equivalent. As almost all the metals interfere with this method, it is necessary to separate them first. It may be noted,

however, that lead and arsenic in large quantities have no effect on the accuracy of this process.

87. IRON (TOTAL), BICHROMATE PROCESS.

Standard : N/10 potassium bichromate (PAR. 57).

Indicator : (External) potassium ferricyanide (PAR. 57).

(1) If flower wire (iron content known) is procurable, dissolve .2 gram in 20 c.cs. hydrochloric acid.

(2) If it is not procurable, to a solution of pure ferric chloride add slight excess of ammonia, boil and allow to settle. Filter, wash thoroughly, separate some of the precipitate from the filter-paper and ignite till constant in weight. Take .3 gram of this product and dissolve in 20 c.cs. hydrochloric acid.

From this point the treatment in either case is identical.

Reduce this solution, diluted to 150 c.cs., with stannous chloride solution till one drop destroys the last trace of yellow colour due to ferric chloride, and add 1 drop only in excess. To the solution, now add 20 c.cs. mercuric chloride, which destroys the excess of stannous chloride, and titrate with the standard till a drop of the solution, added to a drop of the indicator spotted on a porcelain plate, just fails to produce a blue or green colour, indicating that all the ferrous iron has been transformed to the ferric state. Calculate thus—

.2 gram flower wire (99.62 per cent. iron) ; .19924 gram iron consumed 35.4 c.cs.

1 c.c. = .00563 gram iron,

or .3 gram ferric oxide $\times .7 = .21$ gram iron, consumed 37.3 c.cs.

Factor 1 c.c. = .00563 gram iron.

88. IRON (FERRIC).

Standard : stannous chloride (PAR. 65).

Indicator : Methylene blue (PAR. 55).

Dissolve .4 gram of pure freshly ignited ferric oxide (PAR. 87 (2)) in 40 c.cs. hydrochloric acid, and dilute to 250 c.cs.

Pipette off 50 c.cs. of this solution equal to .08 gram ferric oxide, and evaporate to 20 c.cs. bulk. Titrate this solution with the standard solution, till the yellow colour has almost disappeared. Add 10 c.cs. methylene blue and continue titrating, till the blue colour just appears.

Divide .056 (the iron content of .08 gram ferric oxide) by the number of c.cs. consumed, to find the value of 1 c.c. standard solution.

89. IRON (FERROUS).

Standard: N/10 potassium bichrome (PAR. 57).

Indicator: (External) potassium ferricyanide (PAR. 57).

To a flask, fitted with an exit tube and from which the air has been displaced with carbon dioxide, add 1 gram of the salt in which the ferrous iron is to be estimated. Add 40 c.cs. hydrochloric acid and heat on the hot plate till dissolved. Dilute the solution to 200 c.cs. with water, and titrate immediately with the standard, till a spot of the solution, added to a spot of the indicator on a porcelain plate, just fails to produce a blue or green colour.

90. IRON.

Standard: N/10 sodium hyposulphite (PAR. 55)

Indicator: Sodium salicylate (PAR. 55).

.2 gram freshly ignited ferric oxide (PAR. 87 (2)) is dissolved in 20 c.cs. hydrochloric acid and diluted to 150 c.cs. with water. Add 5 c.cs. of a 5 per cent. copper chloride solution in hydrochloric acid, together with 20 c.cs. of the indicator. The deep violet coloration produced is just destroyed by titrating with the standard

solution run in from a burette. The value of 1 c.c. standard is found by dividing .14 gram (the iron content of .2 gram ferric oxide) by the number of c.cs. consumed.

91. MANGANESE, PERSULPHATE METHOD.

Standard : Arsenious acid (PAR. 64).

Indicator : (Internal) colour change.

.2 gram manganese dioxide is dissolved in 20 c.cs. nitric acid, and diluted to 100 c.cs. bulk, 20-30 c.cs. of 1 per cent. solution of silver nitrate and 1 gram ammonium persulphate are added, and the temperature maintained at about 60° C. for 20 minutes. Cool, dilute to 150 c.cs. bulk, and run in the standard solution, from a burette, till the pink colour just disappears.

The value of 1 c.c. standard is found by dividing .1264 by the number of c.cs. consumed.

92. ARSENIC, IODINE METHOD.

Standard : Iodine (PAR. 67).

Indicator : (Internal) starch solution (PAR. 53), or methylene blue (PAR. 55).

Weigh out accurately .66 gram pure arsenious acid into a flask and add 1 gram sodium carbonate and 200 c.cs. water, boiling till the arsenic has dissolved. Cool, add 2 grams carbonate of soda, and dilute to 1 litre.

1 c.c. = .0005 gram arsenic.

Take 20 c.cs. of the above solution, add 20 c.cs. of the indicator, and titrate till a permanent blue colour is produced. 20 c.cs. arsenious acid solution should take 20 c.cs. of the iodine solution to produce this change if the iodine is correct. Suppose, however, 21 c.cs. were used, then

$$1 \text{ c.c.} = \frac{20 \times .0005}{21.0} .000476 \text{ gram arsenic.}$$

93. PHOSPHORUS.

Standard : N/1 sulphuric acid (PAR. 61).

N/1 caustic potash (PAR. 62).

Indicator : (Internal) phenolphthalein (PAR. 62).

Weigh out 1 gram ammonio phospho-molybdate and dissolve by adding 50 c.cs. of normal caustic potash solution. Titrate the excess of caustic potash by means of N/1 sulphuric acid using phenolphthalein as an indicator.

1 c.c. N/1 potash = approximately 0.00044 gram phosphorus. Calculate thus—

50.0 c.cs. caustic potash added

13.0 c.cs. N/1 sulphuric acid used

37.0 = 0.0163 gram phosphorus.

Factor 1 c.c. = 0.00044 gram phosphorus.

94. MAGNESIUM.

Standard : Uranium acetate (PAR. 63).

Indicator : (External) potassium ferrocyanide (PAR. 63).

Dissolve .25 gram magnesium phosphate in slight excess of hydrochloric acid, and add 5 c.cs. sodium acetate solution. Run in standard uranium acetate solution, from a burette, to the cold solution till the reaction is almost complete, then heat to 80° or 90° C., and continue the titration till a drop of the solution, added to a drop of the indicator spotted on a white porcelain plate, gives a faint reddish-brown coloration.

1 c.c. uranium acetate solution = approximately 0.0017 gram magnesium.

95. NICKEL.

Standard : Potassium cyanide silver nitrate (PAR. 68).

Indicator : (Internal) citric acid potassium iodide (PAR. 68).

Weigh out .2 gram pure nickel, dissolve in 30 c.cs. nitric acid water (1-2), add slight excess of ammonia, dilute, cool to 15.5° C., and make up to 500 c.cs. To 100 c.cs. of this solution add 10 c.cs. of the indicator solution, and titrate with the standard silver nitrate cyanide solution till the cloudiness which forms on the first addition just disappears. The end reaction is very distinct.

The value of 1 c.c. is found by dividing .04 gram (the nickel used) by the number of c.cs. consumed.

96. COBALT.

Standard: N/10 sodium hyposulphite (PAR. 55).

Indicator: (Internal) starch solution (PAR. 53); or methylene blue (PAR. 55).

Weigh out .2 gram pure cobalt, or take a solution (the cobalt of which is accurately known) equivalent to .2 gram cobalt. If the solid is used, dissolve in 30 c.cs. nitric acid water (1-2) and dilute to 100 c.cs.

If a solution is taken it must also approximate 100 c.cs. bulk. To the solution of cobalt, add 30 c.cs. 10 per cent. hydrogen peroxide, 60 c.cs. of 50 per cent. sodium hydrogen carbonate solution, and 60 c.cs. caustic soda solution. Stir well, and boil for 20 minutes to destroy the excess of hydrogen peroxide. Cool, destroy the precipitate by adding 1 gram potassium iodide and sulphuric acid, and titrate the liberated iodine by means of N/10 hyposulphite of soda. Divide .2 gram by the number of c.cs. consumed to find the factor.

NOTE.—15 c.cs. of hydrogen peroxide and 30 c.cs. 5 per cent. sodium hydrogen carbonate for every .1 gram cobalt (approximately) present in the sample.

97. URANIUM.

Standard: Sodium hydric phosphate (PAR. 69).

Indicator: Potassium ferrocyanide (PAR. 63).

This method is based on the precipitation of uranium as phosphate from acetic acid solutions and the recognition of complete precipitation by means of potassium ferrocyanide. Dissolve the precipitated sodium uranate in nitric acid and evaporate to small bulk, add 2 grams sodium acetate, dilute to 100 c.cs. with water, and boil.

Titrate the boiling solution with standard sodium phosphate solution, till it ceases to give a brown coloration with the indicator. Multiply the number of c.cs. consumed by the factor found and calculate to per cent.

98. CADMIUM.

Standard: N/10 potassium permanganate (PAR. 70).

Indicator: (Internal) colour change.

The solution containing the cadmium is concentrated by evaporation to 50 c.cs. bulk. Add excess of oxalic acid and 20 c.cs. alcohol, and allow the precipitate to settle. Filter the precipitate and wash with alcohol, till quite free from oxalic acid. Dissolve the precipitate in hot hydrochloric acid solution (1-3), and titrate the liberated oxalic acid by means of N/10 potassium permanganate until a faint pink colour persists after constant stirring. Calculate to per cent. using the factor found in PAR. 70.

99. CHROMIUM, BICHROMATE METHOD.

Standard: N/10 potassium bichromate (PAR. 57).

Indicator: Potassium ferricyanide (PAR. 57).

Dilute the solution containing the chromium to 200 c.cs. and boil, add 10 c.cs. of a 1 per cent. solution of silver nitrate and 10 c.cs. of a cold saturated solution of ammonium persulphate.

On boiling, the chromium is converted into chromate and the excess of persulphate is decomposed. Add 5 c.cs.

hydrochloric acid and boil for 5 minutes. Add .5 gram of iron ammonium sulphate (iron content known), and titrate the remaining ferrous iron by means of N/10 potassium bichromate (PAR. 57).

Subtract the number of c.cs. consumed from that consumed by the .5 gram iron ammonium sulphate, multiply the difference by the factor for iron (PAR. 87), and then by .31 for chromium. Calculate to per cent.

NOTE.—The iron ammonium sulphate may be used in the form of a standard solution, thus saving the labour of weighing out a quantity for each estimation.

100. MANGANESE, IRON AMMONIUM SULPHATE METHOD.

Standard: N/10 potassium bichromate (PAR. 57).

Indicator: Potassium ferricyanide (PAR. 57).

To the solution containing the manganese, add calcium carbonate till neutral, shown by the solution turning reddish, and acidify with a drop or two of hydrochloric acid. Add 2 or 3 grams zinc sulphate and 50 c.cs. of bromine water, and raise the temperature to 60° C. Now add 4 grams of calcium carbonate, stir well, and filter. Test the filtrate with ammonia, to make sure all the manganese is precipitated. Transfer filter-paper and precipitate to a large beaker and add 100 c.cs. sulphuric acid water (1-4). Add iron ammonium sulphate (iron known), and estimate the remaining ferrous iron by the bichromate method. The iron oxidized, multiplied by the factor .491, gives the manganese present.

NOTE.—The iron ammonium sulphate may be added solid or in the form of a standard solution, a fair excess must be added and the solid or the solution should be frequently standardized.

101. BISMUTH.

Standard : N/10 potassium permanganate (PAR. 70).

Indicator : (Internal) colour change.

To the nitric acid solution containing the bismuth, which must not contain free hydrochloric acid or chlorides, add methylated spirits, and a slight excess of oxalic acid, which precipitates bismuth as oxalate. Decant the supernatant liquor carefully, and wash the precipitate six times with hot water by decantation, wash on the filter-paper and continue washing with hot water till completely free from acid. Dissolve the precipitate in dilute sulphuric acid (1-4) and titrate the solution with the standard till a permanent pink colour persists on stirring.

Factor 1 c.c. = .0104 gram bismuth approximately.

102. MANGANESE, SODIUM BISMUTHATE
METHOD.

Standard Solution : N/10 potassium bichromate (PAR. 57).

Indicator : Potassium ferricyanide (PAR. 57).

Cool the solution containing the manganese to the room temperature, add 10 c.cs. nitric acid and oxidize the manganese to permanganic acid by adding excess of sodium bismuthate and stirring thoroughly. Filter off excess of sodium bismuthate, add iron ammonium sulphate (iron known) in excess and complete the estimation of manganese exactly as described in PAR. 100.

103. MOLYBDENUM.

Standard Solution : Lead acetate (PAR. 73).

Indicator : Tannic acid solution (PAR. 56).

The solution containing the molybdenum is made

slightly ammoniacal and then rendered faintly acid with acetic acid. Nitric acid or nitrates should not be present.

This solution is titrated, boiling, with standard lead acetate solution, until a drop of the solution, added to a drop of the indicator, just fails to produce a canary colour. Multiply the number of c.cs. consumed by the factor found in PAR. 73, and calculate to per cent.

104. SILVER.

Standard: Ammonium sulphocyanate (PAR. 71).

Indicator: 5 per cent. solution of iron ammonia alum (PAR. 71).

Dissolve .4 gram pure silver in nitric acid and evaporate, to drive off all nitrous fumes, dilute to 150 c.cs. and add 5 c.cs. of the indicator. If the colour of the ferric salt is apparent, add a little more nitric acid till the colour disappears. Run in the sulphocyanate of ammonium solution from a burette, till near the end of the reaction. Each drop produces a blood red cloud which disappears on shaking. When the point of complete precipitation is approached, the precipitate subsides and the addition of the standard is continued, drop by drop, till the solution assumes a light brown tint, permanent after frequent shakings. Divide .4 gram (sample) by the number of c.cs. consumed to find the factor which should be approximately

Factor 1 c.c. = .01 gram silver.

105. SULPHUR.

Standard: Ammonium molybdate (PAR. 56).

Indicator: Tannic acid (PAR. 56).

The sulphur must be present in the solution in the form of sulphuric acid.

Add to the solution containing the sulphur to be estimated, a slight excess of lead nitrate, boil and add 20 c.cs. methylated spirits. Allow the precipitate to settle, filter, wash thoroughly with hot water, dissolve from the filter-paper with ammonium acetate solution, and titrate with the standard exactly as in the estimation of lead (PAR. 56).

Factor = .001546 gram sulphur approximately.

106. VANADIUM.

Standard: N/10 potassium permanganate (PAR. 70).

Indicator: (Internal) colour change.

The vanadic oxide is dissolved in sulphuric acid, or the solution containing the vanadium is evaporated almost to dryness with sulphuric acid. Add 150 c.cs. water, saturate with sulphur dioxide, and allow to stand for half an hour. Boil off completely the sulphur dioxide and titrate the solution with the standard, till a permanent pink colour persists. Multiply the number of c.cs. consumed by the factor and calculate to percentage.

Factor = .0051 gram vanadium approximately.

107. ALUMINIUM, SEAMON'S PROCESS.

Standard: Sulphuric acid (PAR. 72); caustic potash (PAR. 72).

Indicator: Phenolphthalein (PAR. 62).

Treat the acid solution containing the alumina with 2 grams sodium peroxide, and boil. Filter off the precipitated iron and wash thoroughly. The filtrate contains the alumina as sodium aluminate.

Add 5 c.cs. of phenolphthalein and ordinary dilute sulphuric acid, till a precipitate begins to form which redissolves on stirring, being careful not to pass the neutralization point. Then run in standard sulphuric

acid from a burette till exactly neutralized. It is unnecessary to measure this addition. Add a measured quantity of the standard and heat to boiling, when the solution will become clear. A standard solution of caustic potash is next run in, from a burette, to determine the excess of acid added, being careful to make a fresh addition of phenolphthalein before titrating. The c.cs. of excess acid are deducted from the measured quantity added, from which the weight of alumina is calculated.

Factor = $\cdot 005$ gram Al_2O_3 .

= $\cdot 00265$ gram aluminium.

108. CALCIUM.

Standard: N/10 potassium permanganate (PAR. 70).

Indicator: (Internal) colour change.

The calcium oxalate precipitate, produced exactly as in the gravimetric estimation (PAR. 38), is thoroughly washed. Pierce the filter-paper and wash the precipitate through, into a beaker, and drop dilute hot sulphuric acid round the paper and wash. To the solution, add 5 c.cs. concentrated sulphuric acid and boil. While nearly boiling, titrate with the standard, till a permanent pink colour persists. Multiply by the factor and calculate to per cent.

Factor = $\cdot 0028$ gram CaO approximately.

= $\cdot 0020$ gram calcium approximately.

109. ARSENIC.

Standard: Ammonium sulphocyanate (PAR. 71).

Indicator: Solution of iron ammonia alum (PAR. 71).

To the solution containing the arsenic, add 20 c.cs. of a 1 per cent. solution of silver nitrate, after slightly acidifying with acetic acid, which will precipitate arsenic and any chlorides present. Add ammonia carefully, which

dissolves chloride of silver, leaving the red silver arsenate undissolved. Render the solution feebly acid with acetic acid, add 2 grams ammonium acetate, and boil. Filter off the precipitate, wash free from silver salts, and transfer a clean beaker under the funnel. Dissolve the silver arsenate, with cold dilute nitric acid (1-4), wash with cold water, add 5 c.cs. indicator and titrate with the standard, till a permanent red colour is produced, shaking thoroughly between each addition. The end reaction is very sharp.

Factor = .0025 gram approximately.

110. SULPHUR, BARIUM SULPHATE METHOD.

Standard : Barium chloride (PAR. 74).

Indicator : (External) potassium chromate (PAR. 74).

To the solution containing the sulphur as sulphate, add 2 grams sodium acetate, 2 c.cs. glacial acetic acid, and heat to boiling. Run in the standard from a burette, to the boiling solution, till a drop of the solution, added to a spot of the indicator on a white porcelain plate, gives a pale yellow colour. The same remarks apply about reserving a portion of the solution as in Lead (PAR. 79).

1 c.c. = .005 gram sulphur approximately.

111. TITANIUM.

Standard : N/10 potassium permanganate (PAR. 70).

Indicator : (Internal) colour change.

The oxides containing the titanium are transferred to an Ehrlenmeyer flask, fitted with an exit tube, and completely dissolved in hydrochloric acid (sulphuric acid is to be avoided). The reduction is affected by means of granulated zinc, with or without the application of a gentle heat. The reduction being complete, the solution

is decanted from the zinc, the zinc washed by decantation four times, and the solution titrated with the standard till a faint pink colour persists.

Factor = .00481 gram titanium approximately.

112. BORON.

Standard : Caustic soda solution (PAR. 75).

Indicator : Phenolphthalein (PAR. 62).

To the solution containing the boron, in the form of boric acid, add 2 c.cs. of indicator solution and run in, from a burette, the standard solution, till a certain bluish shade appears, no need to read the burette.

Now add about $\frac{1}{3}$ of the volume of solution of glycerol, 2 c.cs. indicator, and titrate again with the standard till the bluish shade reappears.

Factor 1 c.c. N/10 alkali = .0071 gram boric acid.

= .00126 gram boron.

CHAPTER VIII

COLORIMETRIC ESTIMATIONS, STANDARD SOLUTION, AND INDICATORS

For the estimation of elements present only in small quantities or as impurities, various colorimetric estimations have been devised, the colorimetric or Nessler's colour tubes being used for the comparison of the colours produced. The indicators used to produce the colours must produce them quantitatively, otherwise the process would be useless, and the standard solution should, as far as possible, exist in the same form as the metal to be estimated.

A colorimeter is shown in Fig. 28.

113. IRON, SULPHOCYANIDE METHOD.

Standard Solution: Dissolve 8.606 grams of pure iron alum in distilled water and dilute to 1 litre.

Dilute 10 c.cs. of this solution to 100 c.cs. with distilled water as weaker solutions become turbid on standing.
1 c.c. diluted solution = .0001 gram iron.

Indicator: Solid ammonium sulphocyanide.

114. TIN, MOLYBDENUM TRIOXIDE METHOD.

Standard Solution: Dissolve 1.3 grams of stannous chloride in 20 c.cs. hydrochloric acid and dilute, so that 1 c.c. will equal approximately .001 gram tin; about 1 litre is required. Or make the acid solution of stannous

chloride up to 1 litre and find the value of 1 c.c., by titrating 100 c.cs. with N/10 iodine solution as in PAR. 76.

NOTE.—The standard solution should be kept in a cool place, away from the light, and must be frequently standardized by means of N/10 iodine solution.

Indicator: The indicator solution is made by dissolving

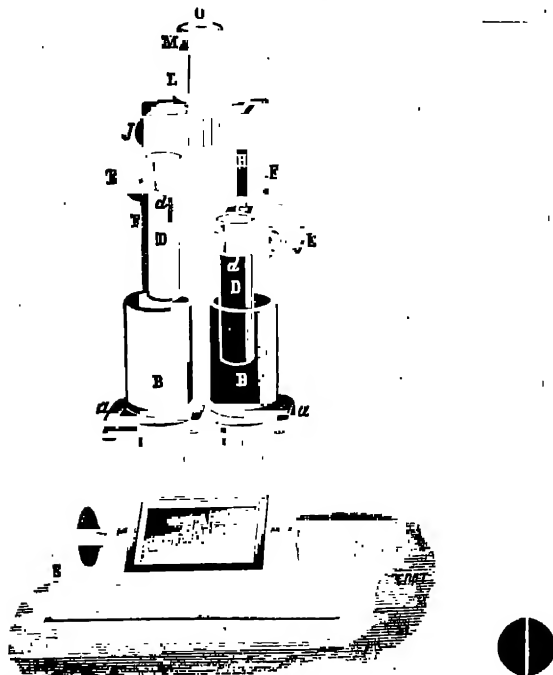


FIG. 28.

1 gram molybdenum trioxide in dilute caustic soda solution, adding hydrochloric acid in slight excess and diluting to 200 c.cs. with distilled water.

115. COPPER.

Standard solution: Dissolve 3.93 grams copper sulphate in distilled water and dilute to 1 litre. This solution

should give an approximate factor of '001 gram copper, but the copper should be estimated in 100 c.cs., by the sodium hyposulphite method (PAR. 85), and the factor noted.

Indicator : Ammonia.

116. VANADIUM.

Standard Solution : Dissolve 1 gram of ammonium vanadate in distilled water, add 20 c.cs. dilute sulphuric acid (1-3), dilute to 1 litre and mix thoroughly. Estimate vanadium in 200 c.cs. of this solution, as in PAR. 25, and dilute so that 1 c.c. equals '0001 gram vanadium.

(1) *Indicator* : Hydrogen peroxide 10 per cent. and phosphoric acid.

(2) Or, in place of hydrogen peroxide, a solution of thymol will be found to give excellent results.

The thymol is dissolved in a little acetic acid and diluted with a 3 per cent. solution of sulphuric acid.

This indicator is colourless and stable, if stored away from direct sunlight.

117. MANGANESE.

Standard solution : Dissolve '287 gram of permanganate of potash in distilled water, acidify slightly with nitric acid and dilute to 1 litre.

1 c.c. = '0001 gram manganese.

Indicator : 1 per cent. silver nitrate solution and solid ammonium persulphate.

118. TITANIUM.

Weigh out '6 gram potassium titanate fluoride, dissolve in a little concentrated sulphuric acid and dilute to 100 c.cs. with 3 per cent. solution of sulphuric acid.

The solution may also be prepared by weighing out 1 gram pure titanium oxide, melting cautiously with

potassium bisulphate till the fusion becomes clear. Cool and dissolve in a 3 per cent. solution of sulphuric acid, make up to a definite volume, pipette off 20 c.cs. and estimate titanium as in PAR. III.

Dilute the remaining solution so that 1 c.c. = .002 gram TiO_2 .

Indicator: Hydrogen peroxide and stannous chloride in hydrochloric acid.

119. NICKEL.

Dissolve 4.79 grams nickel sulphate in distilled water and dilute to 1 litre.

1 c.c. = approximately .001 gram nickel.

To find the factor, dissolve .25 gram pure nickel in nitric acid, add 10 c.cs. sulphuric acid and evaporate to fuming. When cold, dilute with distilled water to 250 c.cs., pipette off 50 c.cs. into a colour tube, and standardize against the standard solution. .05 gram (nickel used) divided by the number of c.cs. consumed gives the factor.

Indicator: Ammonia, and 4 per cent. solution of potassium thiocarbonate.

120. IRON, SODIUM SALICYLATE METHOD.

Standard Solution: Solution of ferric chloride (iron content known) is diluted till 1 c.c. contains .001 gram of iron.

Indicator: 5 per cent. solution of copper chloride in hydrochloric acid, and 10 per cent solution of sodium salicylate.

121. ZINC, RESORCINOL METHOD.

Standard Solution: Dissolve 4.396 grams zinc sulphate in 1 litre of distilled water.

1 c.c. = .001 gram zinc.

Indicator: 5 per cent. solution of resorcinol.

122. LEAD.

Standard Solution : Dissolve 1.831 grams pure normal lead acetate in distilled water, add 10 c.cs. glacial acetic acid, and dilute to 1 litre.

Dilute 10 c.cs. of this solution to 100 c.cs. for use.

1 c.c. = .0001.

Indicator : Pass sulphuretted hydrogen gas through distilled water to saturation.

123. CHROMIUM.

Standard Solution : Dissolve 2.827 grams pure recrystallized potassium bichromate in 1 litre of distilled water.

Indicator : Digest logwood chips in distilled water and decant into a stoppered bottle.

124. MOLYBDENUM.

Standard Solution : Dissolve 10.208 grams of ammonium molybdate in 1 litre of distilled water.

1 c.c. of this solution equals .005 gram molybdenum approximately, but must be tested against a solution in which the molybdenum is accurately known and the factor noted.

Indicator : To 80 c.cs. of a saturated solution of ferrous sulphate, add 20 c.cs. concentrated sulphuric acid, and preserve in a stoppered bottle.

125. BISMUTH.

Standard solution : Dissolve 1 gram pure bismuth in 3 c.cs. of nitric acid, evaporate with 2 c.cs. sulphuric acid, and dilute to 1 litre with distilled water.

1 c.c. = .0001 gram bismuth.

Indicator : Dilute 10 c.cs. of the commercial sulphurous

acid to 100 c.cs. with distilled water. Dissolve in 100 c.cs. distilled water 10 grams of potassium iodide. Preserve both solutions in stoppered bottles.

126. COBALT.

Standard Solution: Dissolve 5.983 grams of cobalt nitrate in 1 litre distilled water.

Indicator: Dissolve 10 grams citric acid in 100 c.cs. distilled water.

Dissolve .1 gram potassium ferricyanide in 100 c.cs. of water.

This solution must be freshly prepared.

127. TUNGSTEN.

Standard Solution: Fuse 1.261 grams tungstic acid with 2 grams potassium bisulphate, dissolve the fusion in ammonium carbonate solution, and dilute to 1 litre with distilled water.

1 c.c. = .001 gram tungsten.

Indicator: Stannous chloride in hydrochloric acid.

128. BORON.

Standard Solution: Dissolve 5.637 grams of boric acid H_3BO_3 in distilled water, add 20 c.cs. hydrochloric acid, and dilute to 1 litre.

Indicator: Digest 5 grams turmeric root and 5 grams tartaric acid in hot alcohol and dilute to 500 c.cs.

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129. IRON, IN MINUTE QUANTITIES.

Standard: Iron alum (PAR. 113).

Indicator: Solid ammonium sulphocyanide (PAR. 113).
The solution in which the iron is to be estimated, is

evaporated to 10 c.cs. bulk, and when cold, transferred to a stoppered test-tube. Add 1 c.c. N/1 sulphuric acid, .2 gram of ammonium sulphocyanide, and 10 c.cs. ether. A red coloration will be produced which, on settling, will be contained in the ether layer. In a similar test-tube, place 10 c.cs. distilled water, add 1 c.c. N/1 sulphuric acid, .2 gram ammonium sulphocyanide, and 10 c.cs. ether. Titrate this solution with the standard, till the colours of the ether layers are equal. Multiply the c.cs. consumed by the factor (PAR. 113), and calculate to percentage.

NOTE.—The tubes should be set aside and used for no other purpose than the estimation of iron by this method, and should be carefully cleaned after each estimation.

130. COPPER.

Standard: Copper sulphate (PAR. 115).

Indicator: Ammonia.

To the solution containing the copper, add 5 c.cs. of sulphuric acid and evaporate almost to dryness. Cool, and dilute with 50 c.cs. of distilled water. Neutralize exactly with ammonia, add 10 c.cs. in excess and dilute to 100 c.cs.

To a similar tube add 60 c.cs. distilled water and 10 c.cs. ammonia. Titrate this solution with the standard, until on diluting to 100 c.cs. with distilled water, the colours are equal. Multiply the number of c.cs. consumed by the factor found in PAR. 115 and calculate to percentage.

131. TIN, MOLYBDATE METHOD.

Standard: Stannous chloride (PAR. 114).

Indicator: Molybdenum trioxide solution (PAR. 114).

To the solution in which the tin has to be estimated, which should be about 60 c.cs. in bulk, add 10 c.cs. of the

indicator solution and dilute to 100 c.cs. with distilled water. A blue coloration is produced.

A blank experiment is prepared by adding to a similar tube 60 c.cs. distilled water, 10 c.cs. hydrochloric acid, and 10 c.cs. indicator solution. Titrate this solution with the standard solution till the colours are exactly equal on diluting to 100 c.cs. Calculate as usual.

132. TITANIUM.

Standard: Titanium sulphate (PAR. 118).

Indicator: Stannous chloride and hydrogen peroxide (PAR. 118).

The oxide of titanium precipitate is dissolved in as little sulphuric acid as possible, 50 c.cs. of distilled water added and the solution transferred to a colour tube. From a pipette, add 5 c.cs. hydrogen peroxide and 5 c.cs. stannous chloride solution, which produces a violet coloration. Dilute to 100 c.cs. with distilled water. To a similar tube, add 60 c.cs. distilled water, add from a pipette, 5 c.cs. hydrogen peroxide and 5 c.cs. stannous chloride. Run in, from a burette, standard titanium sulphate (PAR. 118), till the colours, on diluting to 100 c.cs., are equal. From the number of c.cs. consumed, calculate the percentage of titanium present, using the factor found in PAR. 118.

133. VANADIUM.

Standard: Ammonium vanadate (PAR. 116).

Indicator: Phosphoric acid and hydrogen peroxide (PAR. 116 (1)), or phosphoric acid and thymol (PAR. 116 (2)).

The solution, in which the vanadium is to be estimated, and which must be not more than 60 c.cs. bulk, is transferred to a colour tube, 5 c.cs. phosphoric acid and 5 c.cs. hydrogen peroxide or thymol solution (PAR. 116 (2)).

added from a pipette. The solution is thoroughly mixed and diluted to 100 c.cs. with distilled water. A blank experiment is prepared in a similar colour tube, by adding 60 c.cs. distilled water, 4 c.cs. phosphoric acid and 5 c.cs. hydrogen peroxide or thymol as used in the experiment. Run in, from a burette, standard solution of ammonium vanadate (PAR. 116) until, on diluting to 100 c.cs. with distilled water, the colours are equal. Calculate to vanadium, using the factor found in PAR. 116, and bring to percentage.

134. NICKEL.

Standard : Nickel sulphate (PAR. 119).

Indicator : Potassium thiocarbonate (PAR. 119).

Neutralize the solution containing the nickel, which should be about 60 c.cs. in bulk, with ammonia, add 10 c.cs. ammonia in excess, and transfer to a colour tube. Add 2 c.cs. of a 4 per cent. solution of potassium thiocarbonate, dilute to 100 c.cs. with distilled water, and mix thoroughly.

To about 60 c.cs. distilled water, in a similar colour tube, add 10 c.cs. ammonia and 2 c.cs. of the thiocarbonate solution. Titrate this solution with standard nickel sulphate (PAR. 119) till, on diluting to 100 c.cs. with distilled water, the colours are equal; calculate to percentage from the number of c.cs. consumed, using the factor found in PAR. 119.

135. MANGANESE.

Standard : Manganese nitrate (PAR. 117).

Indicator : Internal colour.

The solution containing the manganese to be estimated is evaporated to about 60 c.cs. bulk, and should not contain hydrochloric acid or chlorides.

Transfer to a colour tube and add 20 c.cs. of a 1 per cent.

solution of silver nitrate and 1 gram ammonium persulphate. The solution is warmed for some time at 60° C., and the colour compared with a blank experiment.

To 60 c.cs. distilled water in a similar colour tube, add 20 c.cs. 1 per cent. solution of silver nitrate and 1 gram ammonium persulphate. Heat to 60° C. and add the standard solution (PAR. 117), and allow to stand two minutes between each addition. The maximum colour is developed in this time, after shaking well. From the number of c.cs. consumed, calculate to percentage, using the factor found in PAR. 117.

136. IRON, IN MINUTE QUANTITIES.

Standard: Ferric chloride (PAR. 120).

Indicator: Copper chloride and sodium salicylate (PAR. 120).

The solution containing the iron, in the form of ferric chloride, is evaporated to about 60 c.cs. bulk, 5 drops of a 5 per cent. solution of copper chloride in hydrochloric acid and 20 c.cs. of a 10 per cent. solution of sodium salicylate are added, the solution transferred to a colour tube and diluted to 100 c.cs. with distilled water. The violet coloration produced is compared thus. To 60 c.cs. distilled water, add 5 drops copper chloride solution, and 20 c.cs. of salicylate of soda solution. Titrate this solution with standard ferric chloride solution (PAR. 120) till, on diluting to 100 c.cs. the colours are equal. Multiply the c.cs. consumed by the factor found in PAR. 120, and bring to per cent.

137. ZINC.

Standard: Zinc sulphate (PAR. 121).

Indicator: Resorcinol (PAR. 121).

The following colorimetric estimation given below is reliable, but is not recommended for works processes,

COLORIMETRIC ESTIMATIONS

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owing to the length of time taken in the estimation. It is only used for the estimation of zinc present in traces.

To the solution containing the zinc, which should be about 90 c.cs. bulk, add 2 c.cs. ammonia and 2 c.cs. of a 5 per cent. solution of resorcinol, dilute to 100 c.cs. and cover with paraffin to exclude oxygen. A blue colour is developed, which attains its maximum after standing 24 hours.

A blank experiment is carried out by adding to 50 c.cs. water, 2 c.cs. ammonia and 2 c.cs. 5 per cent. solution of resorcinol, and running from a burette 1 c.c. of a solution of zinc sulphate (PAR. 121), covering with paraffin as before. After standing for 24 hours, the colours are adjusted. If the standard is deeper in colour, dilute till the colours are equal. If the sample is stronger, pour out some of the solution till the object is attained. Take two examples: Blank was diluted to 65 c.cs.

$$\frac{100 \text{ c.cs.} \times '001}{65}$$

gives the quantity of zinc in the sample, '00154 gram.

Blank experiment, diluted to 100 c.cs., was still found to be too strong; pour out solution from the sample tube till equal. 26 c.cs. poured out.

$$\frac{74 \text{ c.cs.} \times '001}{100}$$

gives the quantity of zinc in the sample, '00074 gram.

138. CHROMIUM.

Standard solution: Potassium bichromate (PAR. 123).

Indicator: Logwood (PAR. 123).

To the solution containing the chromium in the form of chromate, which must not occupy more than 60 c.cs. bulk, and which must be neutral, add 2 c.cs. of acetic acid and dilute to 100 c.cs.

Prepare a blank experiment, by adding to 60 c.cs. distilled water 2 c.cs. acetic acid, and titrating with standard potassium bichromate till the colours, when diluted to 100 c.cs. and comparing in Nessler's tubes, are equal.

If 5 c.cs. of a dilute decoction of logwood are added to each tube before making the bulk up to 100 c.cs., and the tubes placed in a large beaker of boiling water, till the maximum colour has developed, a violet red coloration will be developed which may be easily matched, by titrating the blank with the standard as directed.

139. LEAD IN TRACES.

Standard : Lead acetate (PAR. 122).

Indicator : Sulphuretted hydrogen (PAR. 122).

The solution containing the lead, which must be free from other H_2S metals, is evaporated to 50 c.cs. bulk, rendered alkaline with ammonia, and slight excess of acetic acid added.

Transfer to a colour tube, add 2 c.cs. saturated solution of sulphuretted hydrogen, and dilute to 100 c.cs. If lead is present a brownish or black tint will appear. To a similar tube to that used in the estimation, add 60 c.cs. distilled water, 1 c.c. acetic acid, and 2 c.cs. saturated solution of sulphuretted hydrogen. Add a few drops of standard solution of lead acetate, and mix thoroughly; compare the colours and continue this operation till the same intensity of colour is obtained, shaking well between each addition of the standard. When the solution of the blank experiment is diluted to 100 c.cs. the colours should be exactly equal. Multiply the number of c.cs. consumed by the factor and calculate to percentage.

NOTE.—This process only applies to solution containing traces of lead.

Factor = .0001 gram lead.

140. MOLYBDENUM.

Standard : Ammonium molybdate (PAR. 124).

Indicator : Ferrous sulphate (PAR. 124).

Evaporate the solution containing the molybdenum, in the form of ammonium molybdate, to 60 c.cs. bulk, add 20 c.cs. of the indicator solution and dilute to 100 c.cs. in a colour tube.

To a similar colour tube, add 60 c.cs. distilled water and 20 c.cs. indicator solution, and run in, from a burette, the standard ammonium molybdate solution till, on diluting to 100 c.cs., the blue colour is equal to that of the sample. Multiply the number of c.cs. consumed by the factor found (PAR. 124) and bring to percentage.

Factor 1 c.c. = .005 molybdenum approximately.

141. BISMUTH, IODIDE METHOD.

Standard : Bismuth nitrate (PAR. 125).

Indicator : Potassium iodide (PAR. 125), and sulphurous acid.

To the solution containing the bismuth, which should contain not more than .0075 gram bismuth, add 10 c.cs. potassium iodide, and boil to destroy any liberated iodine. Add 10 c.cs. sulphurous acid, filter, if necessary, into a colour tube, cool, and dilute to 100 c.cs.

To 60 c.cs. distilled water, in a similar colour tube, add 10 c.cs. potassium iodide solution and 10 c.cs. sulphurous acid solution, and titrate with the standard till the yellow colour produced, on diluting to 100 c.cs., equals that of the sample.

Multiply the c.cs. consumed by the factor and calculate to percentage.

Factor 1 c.c. = .0001 bismuth approximately.

142. COBALT.

Standard: Cobalt nitrate (PAR. 126).

Indicator: Citric acid potassium ferricyanide (PAR. 126).

Nickel is first separated, if present, by means of dimethylglyoxime (PAR. 21).

To the filtrate, add 20 c.cs. nitric acid and evaporate to 60 c.cs. bulk, and transfer to a colour tube. Add 5 c.cs. citric acid solution and 5 c.cs. ferricyanide from a pipette, dilute to 100 c.cs., and mix thoroughly.

To 60 c.cs. of distilled water, in a similar colour tube, add 5 c.cs. of each of the indicators, and titrate with the standard till, on mixing thoroughly and diluting to 100 c.cs., the red coloration is equal to that of the sample. Calculate to percentage as usual.

Factor 1 c.c. = .001 gram cobalt approximately.

143. TUNGSTEN.

Standard: Tungstic acid (PAR. 127).

Indicator: Stannous chloride (PAR. 127).

Fuse the precipitate containing the tungstic acid with potassium bisulphate, digest the fusion with a solution of ammonium carbonate, and filter into a colour tube, acidify with hydrochloric acid and dilute to 100 c.cs. Acidify the same quantity of ammonium carbonate water with hydrochloric acid. To both tubes, add 5 c.cs. of the indicator and immerse in a large beaker of hot water. A fine blue colour will be developed in the sample tube. The blank experiment is titrated with the standard till, on diluting to 100 c.cs., the colours are equal.

The number of c.cs. consumed multiplied by .001 (the factor) gives the tungsten content of the quantity taken.

144. BORON.

Standard : Boric acid (PAR. 128).

Indicator : Turmeric solution (PAR. 128).

To the solution containing the boron in the form of boric acid, which should occupy 60 c.cs. bulk, add 2 c.cs. hydrochloric acid and 5 c.cs. turmeric solution, and dilute to 100 c.cs.

Place in a similar colour tube 60 c.cs. distilled water, add 2 c.cs. hydrochloric acid and 5 c.cs. turmeric solution, and run in, from a burette, the standard solution till, on diluting to 100 c.cs., the colours are equal. Calculate to percentage as usual.

Factor 1 c.c. = .001 gram boron.

CHAPTER IX

REFRACTION OF STOCK METALS

THE commercial metals supplied to non-ferrous alloy foundries usually contain from 1 per cent. to 4 per cent. impurities, and often these impurities consist of deleterious matter ; it is always advisable to have a check on all stock metals supplied.

Sampling is the most important feature, as if the sample is not absolutely representative, the analysis will be worthless. Drillings must be taken from a proportionate number of ingots, each ingot being drilled through, or at least $\frac{1}{2}$ of its depth, top and bottom. Filings or sawings should be avoided, for reasons already stated, the sample thus taken is thoroughly mixed and a convenient sample taken by quarterings.

In the case of softer metals which drill out in long strands, each strand should be cut into small pieces before mixing and quartering. Preserve the samples in well-corked bottles.

145. COPPER.

The impurities which may be found are arsenic, antimony, tin, bismuth, iron, lead, nickel, zinc, sulphur and phosphorus. In copper (commercially pure) these elements rarely exceed 1 per cent. to 1.5 per cent., so a 10 gram sample at least must be taken.

(a) TIN AND ANTIMONY.—Dissolve 10 grams sample in as little nitric acid as possible, usually 10 c.cs. of the

acid will be found to be sufficient and evaporate to fastness. Take up again with 5 c.cs. nitric acid and 100 c.cs. water, boil, and allow to settle. Filter through a Swedish filter-paper, wash thoroughly, and treat the precipitate as already described for the separation of tin and antimony (PAR. 45 or PAR. 46).

(b) *Lead*.—To the filtrate from tin and antimony, add 5 c.cs. sulphuric acid, and boil. Add methylated spirits, carefully, till the violent liberation of nitrous fumes has abated, and proceed with the estimation of lead as described in PAR. 1 or PAR. 79.

(c) *Bismuth*.—To estimate bismuth, if found, cool the filtrate from lead (b) and add ammonia till very slightly alkaline, easily recognizable by the marked change in colour, and add potassium cyanide till the blue colour is completely destroyed. Solid powdered potassium cyanide may be added at first, till the colour is almost destroyed, but always finish the process by means of a solution in order to avoid adding too great an excess of cyanide. Pass sulphuretted hydrogen gas through this solution, till the bismuth is completely precipitated. Filter off the black precipitate, dissolve from the filter-paper by passing hot dilute nitric acid (1-4) through it and washing the filter-paper thoroughly. Finish the estimation of bismuth as described in PAR. 3, taking the precautions as there directed.

(d) *Sulphur*.—Dissolve 10 grams sample in as little nitric acid as possible, take up with 5 c.cs. nitric acid and 100 c.cs. water, boil, filter, and wash thoroughly. Neutralize the solution with ammonia, acidify with hydrochloric acid, boil, and precipitate sulphur by means of barium chloride solution in slight excess. Complete the estimation as described in PAR. 30.

(e) *Phosphorus*.—Dissolve 10 grams sample in nitric acid and evaporate off nitrous fumes. Add 20 c.cs.

hydrochloric acid, evaporate to dryness, take up with a further 20 c.cs. hydrochloric acid and again evaporate to dryness. Take up with 10 c.cs. hydrochloric acid and boiling water, add 10 c.cs. nitric acid, and proceed with the precipitation and estimation of Phosphorus as described in PAR. 28 or PAR. 29.

(f) *Arsenic*.—Dissolve 10 grams sample in as little nitric acid as possible and evaporate to expel all nitrous fumes, dilute to 100 c.cs. bulk, and neutralize with caustic soda, add about 1 gram of sodium carbonate, dissolved in a little water, and boil. Filter (washing is unnecessary), and dissolve back into the flask with a little dilute hydrochloric acid, add a slight excess of ammonia, 25 c.cs. magnesia mixture, and allow to stand over night. The precipitate may be treated as described in PAR. 9, or, better still, treated volumetrically as described in PAR. 92.

(g) *Iron*.—Dissolve 10 grams sample in as little nitric acid as possible, boil off nitrous fumes and dilute with 100 c.cs. boiling water, allow to settle, and filter off any tin and antimony oxides. Dilute the filtrate to 300 c.cs. with water, and pass sulphuretted hydrogen gas through this solution, till all the H_2S metals have completely precipitated. It is always advisable to test the filtrate from this precipitate, and if any further precipitation occurs, filter again. Boil off sulphuretted hydrogen gas, add nitric acid, and boil to about 150 c.cs. bulk. Add 10 c.cs. hydrochloric acid, 20 c.cs. ammonium chloride, and add slight excess of ammonia, which precipitates iron. Filter off the precipitate, and preserve the filtrate for nickel and zinc. If the precipitate is appreciable, it may be ignited and weighed, but generally it is advisable to dissolve it from the filter-paper, and treat colorimetrically, as directed in PAR. 129 or PAR. 136.

(h) *Nickel*.—To the filtrate add dimethylglyoxime solution and proceed as directed in PAR. 21, preserving

the filtrate for zinc, or conduct the separation as described in (j).

(i) *Zinc*.—To the filtrate from the nickel add 10 c.cs. sulphuric acid, and boil for 20 minutes to destroy the dimethylglyoxime, add slight excess of ammonia, and precipitate zinc by adding excess of yellow ammonium sulphide. Treat this precipitate as described in PAR. 82, after dissolving from the filter-paper as described in (j).

Alternative method for the separation of—

(j) *Nickel and Zinc*.—To the filtrate from iron (g) add excess of yellow ammonium sulphide, heat to 60° C., and allow to stand at that temperature till the precipitate settles. Filter (washing is unnecessary), and dissolve from the paper by passing dilute nitric acid (1-4) through. Wash thoroughly with hot water. Boil for a few minutes, and precipitate nickel with caustic soda solution (PAR. 20), finishing the estimation as there described and precipitating the zinc in the filtrate by passing sulphuretted hydrogen gas. Filter off the zinc sulphide, redissolve from the filter by passing dilute sulphuric acid (1-4) through, and finish, the estimation as described in PAR. 82.

146. TIN.

The tin of commerce is usually obtained fairly pure, sometimes containing as little as 2 per cent. impurity. The usual impurities which may be looked for are iron, arsenic, sulphur, antimony, lead, bismuth, copper, and phosphorus.

Iron in considerable quantity makes tin hard and brittle. Antimony, arsenic, phosphorus, and bismuth reduce its tenacity, while copper over 5 per cent. makes tin hard and renders it less malleable.

(a) *Antimony*.—Antimony may be estimated direct by dissolving 5 grams sample in hydrochloric acid with frequent additions of small quantities of potassium

chlorate till solution is complete. Add a further quantity of 1 gram of potassium chlorate to ensure the antimony being converted into the antimonie state. Boil off the liberated chlorine completely, which may be shown by moistening a strip of filter-paper in solution of potassium iodide and starch solution and holding over the mouth of the beaker. A blue colour will be developed if chlorine fumes are still being given off. When completely free from chlorine, add 10 c.cs. hydrochloric acid, dilute to 300 c.cs. and, after cooling to the room temperature, titrate with sodium hyposulphite as described in PAR. 78. It is advisable to use N/20 sodium hyposulphite, as the quantity of antimony present is generally very small.

(b) *Lead*.—Digest 10 grams sample in nitric acid water (1-1) till the tin is completely oxidized, and evaporate to small bulk. Take up with 50 c.cs. water, and boil. Allow to settle out, filter through a Swedish filter-paper, and wash thoroughly. To the filtrate, add 10 c.cs. sulphuric acid and evaporate to about 15 c.cs. bulk, dilute to 50 c.cs. bulk, and filter off any lead sulphate precipitate. Treat this precipitate either gravimetrically (PAR. 1) or volumetrically (PAR. 79). Preserve the filtrate for copper.

(c) *Copper*.—Transfer the filtrate from (b) to a Nessler's colour tube, neutralize with ammonia, add 10 c.cs. in excess and proceed with the colorimetric estimation as described in PAR. 130. Preserve the solution for bismuth.

(d) *Iron*.—Digest 10 grams sample with nitric acid water (1-1) till oxidation is complete, and evaporate to small bulk. Add caustic soda solution and sodium sulphide, and digest on the hot plate for some time. Dilute, and acidify the solution strongly with hydrochloric acid, and filter off tin sulphide. From the filtrate, boil off hydrogen sulphide and continue boiling till the bulk of the solution has been reduced to 100 c.cs. Cool, add

excess of ammonia. Filter off the iron, and preserve the filtrate. Treat the hydrated ferric oxide precipitate gravimetrically, as described in PAR. 12, or volumetrically, after dissolving from the filter-paper by means of hot hydrochloric acid solution as described in PAR. 87 or PAR. 90.

(e) *Phosphorus*.—Boil the filtrate from iron (o) till the solution is reduced to 60 c.cs. bulk, add 30 c.cs. ammonia and 20 c.cs. magnesia mixture, and complete the estimation of phosphorus as described in PAR. 29.

(f) *Arsenic*.—Dissolve 5 grams sample in nitric hydrochloric water (1-1-2) till completely dissolved, add slight excess of ammonia and yellow ammonium sulphide, and filter off any precipitate and wash. Digest at a gentle heat for about 30 minutes, add 50 c.cs. magnesia mixture, and proceed with the estimation as described in PAR. 9.

(g) *Bismuth*.—From the colorimetric estimation of copper, the ammoniacal solution in the Nessler's tube is washed into a 300 c.cs. beaker and diluted to 200 c.cs. Add a slight excess of nitric acid, and pass sulphuretted hydrogen gas to saturation. Filter off bismuth sulphide, wash the precipitate thoroughly and dissolve from the paper by passing hot nitric acid water (1-4) through. Proceed with the estimation of bismuth as described in PAR. 3, taking the precautions there mentioned.

(h) *Tungsten*.—25 grams sample are digested in the cold, with frequent agitation, with a solution of ferric chloride containing an equivalent of 40 grams iron, for 24 hours. The heavy black powder which remains undissolved is filtered off, washed with hot water, faintly acidified with hydrochloric acid until free from iron, and the tungsten estimated either gravimetrically (PAR. 37) or volumetrically, as in PAR. 143.

(i) *Sulphur*.—Place 10 grams of the sample in a flask, fitted with a two-holed cork. Through one hole passes

a tube, bent at right angles, and closed at the end by means of a clipped rubber tube, through the other hole passes a tube, a connection to a smaller flask. This connection reaches almost to the bottom of the smaller flask. It is advisable to have two such flasks connected together. In those two flasks place 25 c.cs. of a solution of lead oxide, dissolved in caustic soda. To the sample flask add hydrochloric acid (about 60 c.cs.), make the connections, and distil very gently for 3 hours. The generated sulphuretted hydrogen gas is absorbed by the lead solution.

When the reaction is complete, pass through the flask hydrogen gas, admitted by means of the clipped tube, till the flask is completely freed from sulphuretted hydrogen gas. Dissolve the lead sulphide in nitric acid, add hydrochloric acid, and heat to 60° C. for some time.

Add barium chloride solution, and proceed with the estimation of sulphur as described in PAR. 30.

147. ANTIMONY.

Star antimony, as is usually found in commerce, ranges from 98 per cent. to 99·8 per cent. antimony, and the usual impurities found are arsenic, iron, sulphur, lead, and copper.

(a) *Copper*.—Digest 10 grams sample in nitric acid water (1-1) till the antimony has been completely oxidized, and evaporate to small bulk. Add 60 c.cs. water, in which 2 grams tartaric acid has been dissolved, excess of ammonia, and then ammonium sulphide. Antimony goes into solution, leaving sulphides of copper and lead in precipitation. Filter off the precipitate, dissolve in nitric acid water (1-2), and estimate copper colorimetrically, as described in PAR. 130.

(b) *Lead*.—When copper has been estimated, wash the solution and sediment from the colour tube into a beaker, acidify slightly with nitric acid, add 5 c.cs. sulphuric acid,

and proceed with the estimation of lead either gravimetrically (PAR. 1) or volumetrically (PAR. 79).

(c) *Arsenic*.—To the filtrate from (a) add a slight excess of hydrochloric acid, which precipitates antimony and arsenic as sulphides. Digest with a cold 5 per cent. solution of sodium sulphide, which dissolves the metals, leaving sulphur in suspension, add twice as much 10 per cent. caustic soda solution as was added of sodium sulphide, 20 c.cs. of hydrogen peroxide, and boil. Add $\frac{1}{2}$ of the total bulk of methylated spirits and filter off the precipitated antimony. Boil off methylated spirits, and proceed with the estimation of arsenic, as described in PAR. 9, Magnesia Mixture Method.

(d) *Iron*.—Dissolve 2 grams sample in aqua regia, dilute to 300 c.cs. bulk, and pass sulphuretted hydrogen gas to completely precipitate H_2S metals. Filter through a large filter-paper, from the filtrate boil off H_2S and evaporate to 100 c.cs. bulk. Add 5 c.cs. nitric acid, boil to oxidize the iron and precipitate with ammonia in excess. Estimate iron gravimetrically, as in PAR. 12, volumetrically, PAR. 87, or colorimetrically, as in PAR. 129.

(e) *Sulphur*.—Sulphur is best estimated in antimony by the method described under the heading "Sulphur," in the refraction of Tin (PAR. 146 (i)).

148. LEAD.

Lead is usually sold either as hard lead or soft lead. Soft lead is found in commerce containing as much as 99.8 per cent. lead, and the impurities, which may consist of silver, copper, bismuth, cadmium, antimony, arsenic, nickel, iron, zinc, and manganese, are so minute in quantity as to be negligible. If the sample contains 99.8 per cent. lead a refraction is, under ordinary working conditions, unnecessary. Hard lead may be found in commerce

varying between 95 per cent. and 98 per cent. lead, and a refraction is conducted as follows.

(a) *Tin and Antimony*.—10 grams of the sample are taken and digested in 50 c.cs. nitric acid water (1-3), till the soluble portion has completely dissolved. The oxides tin and antimony are filtered, washed thoroughly, and the separation and estimation of tin and antimony conducted as described in PAR. 45. The filtrate is preserved and treated thus—

(b) *Hydrogen sulphide metals*.—Lead is separated from the filtrate by adding 15 c.cs. of sulphuric acid and evaporating to 25 c.cs. bulk, cool, dilute to 150 c.cs., boil for some time, allow the lead sulphate precipitate to settle, filter, and wash thoroughly. Dilute the filtrate to 300 c.cs. with cold water and pass sulphuretted hydrogen gas through this solution and filter off sulphides. It is always advisable to test this filtrate by again passing sulphuretted hydrogen gas, and if any precipitation occurs, add to the first precipitate obtained. This precipitate may contain copper, bismuth, cadmium, arsenic, and silver. The precipitate is dissolved in nitric acid water (1-3), and the two filtrates added together and preserved. The separation of the metals precipitated is conducted as follows:—

(c) *Copper*.—The solution is filtered (if necessary) into a Nessler's tube, and the copper is estimated colorimetrically, as described in PAR. 130.

(d) *Bismuth*.—The solution is now transferred to a beaker, carefully neutralized with nitric acid, the blue colour of the copper is just destroyed with a solution of potassium cyanide, and the bismuth is precipitated with ammonium carbonate, as described in PAR. 3, taking the necessary precautions therein detailed.

(e) *Silver*.—To the filtrate from (d) add 2 c.cs. hydrochloric acid, which precipitates silver as chloride, which may be filtered through a previously dried and weighed

filter-paper and weighed as silver chloride. Factor = $\cdot 7527$ silver, or the silver sulphide formed may be dissolved in boiling nitric acid and treated volumetrically, as described in PAR. 104.

(f) *Arsenic*.—Boil the filtrate from (e) to 100 c.cs. bulk, add ammonia and magnesia mixture, which precipitates arsenic, complete the estimation of arsenic as described in PAR. 9.

(g) *Cadmium*.—The cadmium is estimated in the filtrate from (f), as described in PAR. 36 or PAR. 98 as desired.

(h) *Iron and Nickel*.—The filtrates from the sulphuretted hydrogen precipitates are mixed and boiled thoroughly to expel H_2S , and evaporated to small bulk. Iron and nickel are then precipitated by boiling with caustic soda solution, filtering and washing thoroughly. The precipitate thus obtained is treated as described under the separation of iron and nickel (PAR. 52), and the filtrate preserved for zinc.

(i) *Zinc*.—Sulphuretted hydrogen gas is passed through the filtrate from iron and nickel, till the zinc is completely precipitated as zinc sulphide. Filter this precipitate (washing is unnecessary), allow to drain thoroughly and redissolve from the filter-paper by passing dilute sulphuric acid (1-4) through, and estimate zinc either gravimetrically (PAR. 17) or by either of the volumetric processes described in PARS. 82, 83 or 84.

149. ZINC.

Commercial zincs always contain iron and lead, and many contain tin and cadmium. Copper is not often found, and arsenic less frequently than is generally supposed. Nickel and manganese are found rarely, and then only in extremely minute quantities. Sulphur is usually present, but only in traces as a rule, and aluminium rarely;

but occasionally a parcel of zinc, which has been recovered from the galvanizing tanks, gets upon the market and contains aluminium in appreciable quantity.

(a) *Tin*.—Dissolve 10 grams sample, by adding 50 c.cs. water and 30 c.cs. nitric acid carefully. Heat gently at first, and evaporate to fastness. Take up with 10 c.cs. nitric acid and 120 c.cs. water, and boil. Allow to settle, filter off any precipitate and estimate tin either gravimetrically (PAR. 6) or volumetrically (PARS. 76 or 77). Preserve the filtrate.

(b) *LEAD, COPPER, CADMIUM AND ARSENIC*.—Dilute the filtrate from tin to 250 c.cs. and pass sulphuretted hydrogen gas till all the H_2S metals are completely precipitated. Filter off the sulphides, wash and preserve the filtrate.

(c) *Copper*.—Redissolve the sulphide precipitate, by passing boiling dilute nitric acid (1-3) through the paper, wash thoroughly, transfer the solution to a Nessler's tube and estimate copper colorimetrically, as in PAR. 130.

(d) *Lead*.—Transfer the solution to a beaker, neutralize with nitric acid and add 2 c.cs. sulphuric acid. Evaporate this solution to about 10 c.cs. bulk, dilute to 60 c.cs. with water, boil, allow to settle, and estimate lead as described in PAR. 1.

(e) *Arsenic*.—To the filtrate from lead, add ammonia in excess and magnesia mixture to precipitate arsenic. Complete the estimation as described in PAR. 9.

(f) *Cadmium*.—Estimate cadmium in the filtrate from arsenic as described in PAR. 36 or PAR. 98, as desired.

(g) *Iron and alumina*.—Boil the filtrate from the sulphide metals till H_2S is completely driven off, evaporate to 150 c.cs., and precipitate iron and alumina by the acetate method (PAR. 13).

Separate the iron and aluminium in the precipitate by the method described in PAR. 39.

(h) *Manganese*.—Cool the filtrate from iron and alumina, add bromine till a light port wine colour is produced, allow to stand for one hour, add slight excess of ammonia and if any precipitate is formed estimate the manganese gravimetrically (PAR. 19) or colorimetrically, as in PAR. 135.

(i) *Nickel*.—To the filtrate from the manganese add 10 c.cs. of a 5 per cent. dimethylglyoxime solution, and if any precipitate forms, proceed with the estimation of nickel as described in PAR. 21.

(j) *Sulphur*.—Estimate sulphur in 10 grams sample as described under the heading of Sulphur in the refraction of tin (PAR. 146 (i)).

150. ALUMINIUM.

Commercial aluminium may be obtained of 99.6 per cent. purity, but more often runs between 98 per cent. and 99 per cent. Impurities usually found consist of iron and silicon, and sometimes traces of magnesium, lead, tin, zinc, copper and cadmium.

(a) Dissolve 10 grams sample in strong caustic soda solution, dilute to 200 c.cs., and boil. Any insoluble will consist of lead, copper, cadmium, iron and magnesium. Filter off the insoluble, wash thoroughly and preserve the filtrate.

Ignite the precipitate and redissolve in nitric-hydrochloric water (1—1—2).

(b) *Copper*.—Estimate by the colorimetric method described in PAR. 130.

(c) *Lead*.—Wash the solution from the colour tube, neutralize with nitric acid, add 2 c.cs. sulphuric acid, and proceed with the estimation of lead as described in PAR. 1 or PAR. 79.

(d) *Cadmium*.—Separate the copper and cadmium by adding slight excess of ammonia, decolorizing the solution

by means of a solution of potassium cyanide, diluting to 200 c.cs., and precipitating cadmium by means of sulphuretted hydrogen gas. Complete the estimation of cadmium as described in PAR. 35.

(e) *Iron*.—To the filtrate from copper and cadmium, add 20 c.cs. ammonium chloride and excess of ammonia, which precipitates iron. Estimate either gravimetrically (PAR. 12), colorimetrically (PAR. 129), or volumetrically (PAR. 87), as desired.

(f) *Magnesium*.—To the filtrate from iron, add excess of sodium phosphate solution, stir thoroughly, and estimate magnesium as described in PAR. 32.

(g) *Zinc*.—Dilute the caustic soda filtrate from (a) to 250 c.cs. Pass sulphuretted hydrogen gas through this solution, which will precipitate zinc as zinc sulphide, with some aluminium sulphide. To prevent an appreciable amount of aluminium sulphide being formed, stop the flow of gas when a skin forms where the gas bubbles first. If this is done carefully the small amount of aluminium sulphide formed will not affect the manipulation of the process. Filter off the precipitate (no need to wash), allow to drain thoroughly, dissolve in dilute sulphuric acid (1-4), and proceed with the volumetric estimation of zinc as described in PARS. 82, 83, 84, as desired.

(h) *Silicon and Tin*.—Dissolve 10 grams sample in 50 c.cs. water and 30 c.cs. nitric acid and evaporate to dryness without baking. Take up with 10 c.cs. nitric acid and 100 c.cs. water, filter off the tin oxide and silicon and wash thoroughly.

Wash the precipitate from the paper, using as little water as possible, dissolve the tin by digesting on a hot plate with hydrochloric acid, using small quantities occasionally of potassium chlorate to assist solution, and filter off the remaining silica. Wash, ignite, and weigh.

Factor = .46703 silicon.

(i) *Tin*.—Estimate tin in the filtrate as described in PAR. 5, or, preferably, proceed as in (h) till the point where the precipitate is washed from the paper, evaporate to dryness without baking, dissolve the tin oxide by heating to 60° C. till completely dissolved, with the aid of potassium chlorate, only if absolutely necessary, and proceed with the estimation of tin volumetrically, as described in PARS. 76 or 77, as desired.

151. NICKEL.

Commercial metallic nickel contains about 97 to 98 per cent. nickel, as a rule, and in addition to some cobalt, copper, tin and iron may contain traces of arsenic, antimony, magnesium, aluminium, silicon and sulphur.

(a) *Silicon*.—Dissolve 10 grams sample in 60 c.cs. nitric acid water (1-1), and evaporate to dryness; take up with 10 c.cs. nitric acid and 100 c.cs. water, boil, allow to settle, filter and wash thoroughly. Preserve the filtrate. Wash the precipitate from the paper with as little water as possible, dissolve in hydrochloric acid with the aid of a few crystals of chlorate of potash, adding a few crystals at a time till the tin has completely dissolved. Filter off the precipitate of silicon, ignite and weigh as silica, SiO_2 . Factor = .46703.

(b) *Tin*.—Tin is estimated in the filtrate from the tin and silicon solution in hydrochloric acid, as described in PAR. 5.

(c) *Copper, Arsenic, and Antimony*.—Through the nitric acid filtrate (a) pass sulphuretted hydrogen gas to saturation, which precipitates out any copper, arsenic, or antimony.

(d) *Copper*.—Filter off the precipitate, and wash with water containing a little sulphuretted hydrogen water. Dissolve the precipitate in nitric acid water (1-2), add ammonia and yellow ammonium sulphide which dissolves

antimony and arsenic, leaving copper sulphide in precipitation. Filter off the copper sulphide, wash with water containing a little sulphuretted hydrogen water, ignite, and redissolve the precipitate in nitric acid. Estimate the copper by the colorimetric process described in PAR. 130.

(e) *Antimony and Arsenic*.—Acidify the filtrate from ammonium sulphide slightly with nitric acid, which precipitates antimony and arsenic in the form of sulphide. Conduct the separation of these metals as described in PAR. 47.

(f) *Iron and Alumina*.—From the filtrate from the sulphide metals boil off sulphuretted hydrogen gas and evaporate to 200 c.cs. Add 20 c.cs. ammonium chloride and slight excess of ammonia, which precipitates out iron and alumina. Filter off this precipitate and conduct the separation of iron and alumina as described in PAR. 39.

(g) *Cobalt*.—To the filtrate from iron and alumina add excess of a 5 per cent. solution of dimethylglyoxime and digest at 60° C., till the nickel precipitate settles out, filter and wash thoroughly, add nitric acid in excess and boil for half an hour to destroy dimethylglyoxime, add slight excess of ammonia and precipitate cobalt by adding ammonium sulphide, preserve the filtrate. Redissolve the cobalt sulphide from the filter paper by means of dilute nitric acid (1-3), and proceed with the estimation of cobalt as in PAR. 22 or PAR. 23.

(h) *Magnesium*.—From the ammonium sulphide filtrate from cobalt boil off ammonium sulphide, and evaporate to 100 c.cs. bulk. Add a fair excess of ammonia, and proceed with the estimation of magnesium as described in PAR. 32.

(i) *Sulphur*.—Dissolve 10 grams sample in nitric acid water (1-2) and evaporate to small bulk. Take up with 200 c.cs. of water, neutralize with ammonia exactly, add 10 c.cs. of hydrochloric acid, and boil. Precipitate sulphur by adding barium chloride solution and completing the estimation as described in PAR. 30.

CHAPTER X

ALLOYS

SINCE the middle of the year 1915 several metal substitutes have been adopted to replace the alloys in common use before that time. For instance, in Germany, certain copper base alloys were replaced by zinc alloys containing only 4-5 per cent. copper and 2-3 per cent. aluminium. Cast iron and zinc replaced copper base alloys for certain railway carriage work, brake handles, door handles, etc.

Certain zinc alloys replaced the high-class tin base bearing metals, and alloys containing metallic calcium and lead were used.

Since the advent of the aeroplane several new alloys have come into vogue containing tungsten, vanadium, molybdenum and chromium. Reliable methods for the estimation of these metals are included.

152. COPPER BASE ALLOYS.

Alloys may be found containing, besides copper, one or more of the following elements as constituents of the alloy, along with any of the impurities which may have been added, inadvertently, with the stock metals.

Alloys.—Copper, tin, zinc, lead, nickel, manganese, iron, aluminium, silicon and phosphorus.

Impurities.—With the exception of copper, any of the above metals may be present as impurities with cadmium, arsenic, sulphur, and cobalt.

For the estimation of the metals present as impurities,

the scheme detailed under refraction of metals may be used, and for the general analysis of alloys the following processes are recommended as speedy, accurate works processes.

(a) *Copper*.—In the case of high copper content alloys (over 50 per cent.) .2 gram sample is taken, or, better still, 1 gram sample taken, dissolved in as little nitric acid as possible, filtered, the filter-paper washed thoroughly, and the filtrate diluted to 500 c.cs. An aliquot part equal to .2 gram is pipetted off and evaporated to small bulk.

Dissolve .2 gram sample in as little nitric acid as possible and drive off nitrous fumes. To this solution or an aliquot part evaporated, add 20 c.cs. concentrated sulphuric acid, cover the beaker with a watch-glass and evaporate till dense white fumes are given off, without any trace of nitrous fumes being present, cool carefully, add 80 c.cs. of water, and filter if necessary. Bend a piece of sheet aluminium (about 1 inch broad), at right angles, to fit into the beaker and allow the cover to fit, place it in the solution and allow to digest slowly, till the chocolate-coloured precipitate, deposited on the aluminium, all falls off, leaving the aluminium perfectly clean and the supernatant liquor perfectly clear without any trace of blue colour. Wash the aluminium, allow the precipitate to settle and decant the supernatant liquor through a glass wool filter.

Wash the precipitate four times by decantation with hot water and transfer the beaker containing the precipitate under the funnel, and pour boiling strong nitric acid through the glass wool. It is also advisable to drop a little nitric acid over the aluminium plate through the glass wool. Wash the glass wool and boil the filtrate till the precipitate has dissolved and the nitrous fumes are driven off, neutralize carefully with ammonia, add a drop or two in excess, boil, and render slightly acid with glacial acetic acid, boil

again, dilute to 50 c.cs. and proceed with the estimation of copper (PAR. 85).

The complete precipitation of the copper is easily recognizable as the aluminium has a distinct grey appearance until such is the case, after which it turns quite white.

(b) TIN.—Dissolve 1 gram sample in as little nitric acid as possible, evaporate to fastness, *i.e.*, not quite dry, take up with 5 c.cs. nitric acid, 50 c.cs. water, add 3 c.cs. saturated mercuric chloride solution, boil, and allow to settle. Filter through a fine filter-paper and wash thoroughly. Preserve the filtrate.

(1) *Gravimetric estimation*.—Ignite at a low temperature first, till the filter-paper is completely burnt off, gradually increasing the temperature to redness, cool in a desiccator, and weigh. If no silica or antimony is present calculate the tin oxide (SnO_2) thus obtained to tin. Factor = .78738 tin.

Or (2) *Volumetric estimation*.—Wash the oxide of tin from the filter-paper, using as little water as possible, evaporate to dryness, without baking, dissolve in 40 c.cs. concentrated hydrochloric acid, cover the beaker with a watch-glass, reduce the tin to the stannous state by means of a bent iron nail inserted into the solution as previously described in PAR. 76, digest on a hot plate, at about 60°C ., for fully half an hour, and complete the estimation of tin as already described in PAR. 76 or PAR. 77, as desired.

(c) *Antimony*, (1) (*Gravimetrically*).—In copper base alloys, antimony never occurs unless as an impurity, through using scrap metals in the manufacture, but if found may be estimated thus.

Use 10 grams sample and proceed as in the estimation of tin (volumetric), preserving the filtrate from the oxides, till the point is reached at which the oxides are dissolved in concentrated hydrochloric acid. To this solution add

1 gram freshly precipitated copper, and proceed with the estimation of antimony as described in PAR. 45.

Or (2) (*Volumetrically*).—To the hydrochloric acid solution of the oxides of tin and antimony add 50 c.cs. water, and 10 c.cs. hydrogen peroxide, and boil for half an hour, keeping the bulk constant by frequent additions of boiling water, and proceed with estimation of antimony as described in PAR. 78.

(d) *Lead*.—Estimate in the filtrate from tin (b) as follows. Add 5 c.cs. of sulphuric acid, and boil thoroughly. Add methylated spirits carefully, a few drops at a time, till the violent reaction, due to the liberation of nitrous fumes, has abated, and continue till all the red nitrous fumes have been given off, make up the solution with $\frac{1}{8}$ of its original bulk of methylated spirits, boil gently, and allow to settle.

(1) *Gravimetric estimation*.—Filter through a fine filter-paper and wash thoroughly with water containing $\frac{1}{8}$ of its bulk of methylated spirits. If a large precipitate is obtained, dry, separate, and proceed as described in PAR. 1. If a minute precipitate is obtained, dry, ignite direct, and treat with sulphuric acid as described under the treatment of the filter-paper before igniting the precipitate, PAR. 1.

(2) *Volumetric estimation*.—Proceed as in (1) until the methylated sulphuric precipitate has settled. Filter carefully by decantation, keeping as much of the precipitate in the beaker as possible, wash four times by decantation with hot water, and wash the filter paper thoroughly. Transfer the beaker containing the precipitate under the filter funnel, and dissolve any precipitate from the filter-paper by copious washings with ammonium acetate solution already described. Boil to dissolve the precipitate left behind and complete the estimation of lead as described in PAR. 79.

(c) *Iron and Alumina*.—Both of these metals are occasionally found in the composition of the alloy, and iron is generally found in traces or even up to .25 per cent. as an impurity; aluminium is not so generally found as an impurity.

(1) *Iron*.—Dilute the filtrate from the oxides, in the estimation of antimony, to 300 c.cs. and pass sulphuretted hydrogen gas through this solution till the sulphide metals are all precipitated. Filter off any precipitate, and test the filtrate by again passing the gas. If no further precipitation occurs, boil the filtrate till sulphuretted hydrogen has been completely boiled off, add 10 c.cs. hydrochloric acid, 5 c.cs. nitric acid, and again boil, to completely oxidize any iron and alumina and to free the solution from precipitated sulphur.

Add 10 c.cs. ammonium chloride solution and excess of ammonia, which precipitates iron and alumina. Filter off any precipitate, and wash with hot water, and preserve the filtrate. Redissolve the precipitate from the paper by passing hot dilute hydrochloric acid (1-3) through, wash the paper free from all traces of yellow colour, and precipitate iron by adding caustic soda solution in slight excess. Filter off the iron and estimate either gravimetrically, as described in PAR. 12, volumetrically, as in PAR. 87, or colorimetrically, in PAR. 129 or 136, as desired. Usually one of the colorimetric methods is preferable.

(2) *Alumina*.—The filtrate from the caustic soda solution is acidified with hydrochloric acid, 5 c.cs. nitric acid added, and the estimation of alumina carried out as described in PAR. 14 or 15, whatever process is the most suitable.

(f) *Zinc*.—Estimate zinc in the filtrate from iron and alumina as follows. If the zinc content is under 10 per cent., as in steam metals, etc., use the whole of the filtrate,

otherwise dilute the filtrate to 500 c.cs. and take an aliquot part, equal to about that amount of zinc approximately. To the solution add yellow ammonium sulphide in excess, and boil. After the bulky precipitate has settled, filter through a fairly coarse filter-paper, decanting the clear supernatant liquor first, otherwise the filtration is exceedingly slow. Before washing the precipitate into the filter-paper, it is advisable to remove the filtrate from under the funnel, as it would necessitate the refiltration of all the solution if any of the zinc sulphide came through the filter, as sometimes happens. If the bulk of the filtrate is removed and any of the precipitate came through it would only mean the refiltering of a few c.cs.

Wash the precipitate into the paper and allow to drain thoroughly. Dissolve the precipitate from the paper by passing hot dilute sulphuric acid (1-4) through, using the same solution several times to ensure complete solution, and wash thoroughly with boiling water.

Estimate zinc in this solution by the process described in PAR. 17, gravimetrically, or PAR. 82, volumetrically.

(g) *Manganese*.—In manganese bronzes, the manganese seldom exceeds 4 per cent., and is usually found in conjunction with iron. Take 2-5 grams sample according to the expected content of manganese. Dissolve the sample in as little nitric acid as possible and evaporate off nitrous fumes. Take up again with 5 c.cs. nitric acid and 60 c.cs. water, boil, and allow to settle, filter through a fine filter-paper, and wash thoroughly. Pass sulphuretted hydrogen gas through the filtrate diluted to 250 c.cs., taking the precaution described in (e), filter off the precipitate, and wash thoroughly. Boil down to 100 c.cs. bulk and conduct the separation of iron and manganese as described in PAR. 40. Complete the estimation volumetrically (PAR. 100 or 102) if desired.

(h) *Nickel*.—Nickel is found in various proportions in these alloys, sometimes as high as 25 per cent. nickel content, consequently .5 gram to 2 gram sample should be taken, according to the approximately estimated content of nickel. Dissolve the sample taken, using as little nitric acid as will ensure complete solution, and evaporate almost to dryness. Take up with 5 c.cs. nitric acid and 60 c.cs. water, boil, and allow to settle. Filter off any precipitate and wash the filter-paper thoroughly. To the filtrate add very slight excess of ammonia, and if any precipitate forms, filter off and wash thoroughly, add slight excess of a 5 per cent. solution of dimethylglyoxime and estimate nickel either gravimetrically (PAR. 21) or redissolve the washed precipitate in hot dilute nitric acid (1-3) and estimate nickel volumetrically, as described in PAR. 95. If the caustic soda precipitation of nickel is conducted, sulphuretted hydrogen metals must first be separated, sulphuretted hydrogen boiled off, and the nickel precipitated as described gravimetrically in PAR. 21, or volumetrically in PAR. 95.

(i) *Silicon*.—Silicon is sometimes found in the composition of the alloy, but more often as an impurity.

Dissolve 5 grams of the sample in as little nitric acid as possible, add 20 c.cs. hydrochloric acid and evaporate to dryness. Take up with 5 c.cs. nitric acid and 10 c.cs. hydrochloric acid and again evaporate to dryness. Take up with 5 c.cs. nitric acid and 100 c.cs. water, boil and filter off any precipitate. Wash thoroughly, ignite and weigh as silica. Factor = .46703 silicon.

(j) *Phosphorus*.—An alternative method for the estimation of phosphorus is conducted as described in (k) which will be found to give very accurate results.

Dissolve 5 grams sample in as little nitric acid as possible, add 20 c.cs. hydrochloric acid and evaporate to small bulk. Take up with 5 c.cs. nitric acid and 200 c.cs.

water and pass sulphuretted hydrogen gas to saturation. Filter, test the filtrate as previously recommended, if any more precipitate falls, filter off, wash both precipitates with cold dilute H_2S water and add the washings to the filtrate. Boil down to about 60 c.cs. bulk, add 10 c.cs. nitric acid, boil again, and neutralize with ammonia. Add 5 c.cs. nitric acid, and precipitate phosphorus by the molybdate method (PAR. 28), the combination method (PAR. 29), or the volumetric method (PAR. 93), as desired.

Alternative method—

(k) *Phosphorus*.—To the filtrate from the silicon add 10 c.cs. of a solution of 1 gram cerium chloride in 25 c.cs. hydrochloric acid, and dilute to 250 c.cs. Run in, from a burette, ammonia, till a greenish blue coloration appears, add 4 c.cs. acetic acid, and boil for 10 minutes. Filter by decantation, and wash the precipitate four times, also by decantation, and dissolve the precipitate in the beaker by adding 15 c.cs. nitric acid and 3 c.cs. hydrochloric acid, and precipitate phosphorus by the molybdate method (PAR. 28), or by the combination magnesia mixture method (PAR. 29).

(l) *Chromium*.—Chromium is sometimes found in bronzes in small proportions and may be estimated thus. Dissolve 2 grams sample in 25 c.cs. of aqua regia and add 40 c.cs. sulphuric acid dilute (1-1), cover the beaker with a watch-glass and evaporate till dense white fumes are given off. Cool, dilute to 200 c.cs. with water and boil vigorously. Without troubling about any lead sulphate, remove the copper and any antimony present by digesting with iron wire, and filter into an Ehrlenmeyer flask, add 2 c.cs. of a 1 per cent. silver nitrate solution and 10 c.cs. cold saturated solution of ammonium persulphate. On boiling, the chromium is converted into chromate and the excess of persulphate is decomposed, add 5 c.cs. hydrochloric acid, and boil a little longer. When the solution

has cooled to the room temperature, estimate the chromium volumetrically, as described in PAR. 99.

The above scheme of analysis covers the metals usually found in the copper base alloys, and the impurities found may be estimated as described under their various headings in the refraction of metals.

153. BEARING METAL ALLOYS.

The white bearing metal alloys usually consist of three or more of the following metals:—tin, antimony, lead, copper, nickel, zinc, and bismuth.

Bismuth is not so prominent as formerly, and nickel is coming more into vogue in high-class bearing alloys for high speed and heavy loads.

Among the impurities may be found traces of iron, aluminium, cobalt, manganese, and sulphur, along with any of the other metals mentioned above, not entering into the composition of the alloy.

The alloys are usually classified into lead base, tin base, copper hardened, nickel hardened, cupro nickel hardened, and zinc base groups. The chemical analysis may be speedily and accurately carried out as follows.

(a) *Tin*.—For the estimation of tin in alloys of over 30 per cent. tin takes .2 gram sample, and under 30 per cent. content takes .5 gram. Place the sample in a perfectly dry beaker covered with a watch-glass, add 40 c.cs. concentrated hydrochloric acid, and digest on a hot plate till solution is completed. Sometimes it is necessary to add a crystal or two of potassium chlorate to assist solution, but it is advisable to avoid this, if possible, and in case of necessity only add just the amount required. Insert into this solution a 5-inch nail, bent at right angles so that the cover will fit into place, and digest

again on the hot plate till the tin is completely reduced to the stannous state.

This is usually complete in 30 minutes, and the copper and antimony precipitated in the metallic form.

Proceed with the volumetric estimation of tin as described in PAR. 76 or 77.

(b) *Antimony*.—Digest .5 gram of sample in 20 c.c. of nitric acid water (1-2), till the soluble portion has been dissolved and the oxides of tin and antimony are precipitated. Add 10 drops of saturated solution of mercuric chloride and 50 c.c. of water, boil and allow to settle. Filter off the precipitate, wash thoroughly and preserve the filtrate. The precipitate is washed from the filter-paper into the original beaker and the estimation of antimony carried out as described in PAR. 78.

(c) *Lead*.—To the filtrate from the antimony add 5 c.c. sulphuric acid and boil. Add methylated spirits carefully, till the violent liberation of nitric fumes abates, and dilute the solution with $\frac{1}{2}$ of its original bulk of methylated spirits, and boil gently. When the precipitated lead sulphate has completely settled, decant the clear supernatant liquor, wash the precipitate several times by decantation and transfer the beaker and precipitate under the filter-paper, which has been previously washed thoroughly. Dissolve any precipitate which has inadvertently been poured on the paper, by means of copious washing with boiling ammonium acetate solution, boil to dissolve the precipitate left behind in the beaker and proceed with the estimation of lead by the ammonium molybdate method as described in PAR. 79. In silico alloys of tin, antimony, and lead, such as linotype, statuary type, or bearing metals of the magnolia class, the analysis may be completed accurately, in four hours from commencement by the foregoing processes.

(d) *Copper*.—The quantity taken varies from .5 to 1.0 gram.

to 5 grams according to the copper content, which varies between .5 per cent. and 10 per cent. in bearing metals. Under 1 per cent. take 5 grams sample and over 6 per cent. take .5 gram sample.

Digest the sample taken in nitric acid water (1-1) till the soluble portion has dissolved, using as little acid as possible; evaporate to small bulk, add concentrated sulphuric acid (20 c.cs.) and digest on the hot plate till dense white fumes are given off; completely free from brown nitrous fumes. Cool, dilute to 80 c.cs., filter through a fine filter-paper, and wash thoroughly. Precipitate copper in metallic form by means of an aluminium plate as directed in PAR. 152 (a), and estimate copper by the sodium hyposulphite method as directed in PAR. 85.

(e) *Nickel*.—(1) Digest 1 gram sample in nitric acid water (1-1) till the soluble portion has dissolved. Filter off the oxides of tin and antimony, and wash thoroughly with hot water. Add about 1 gram tartaric acid and neutralize with ammonia carefully. Add slight excess of dimethylglyoxime. Complete the estimation of nickel gravimetrically, as in PAR. 21, or volumetrically, as in PAR. 95.

(2) Proceed as in (e) (1) till the point at which the tin and antimony oxides are filtered and washed. Dilute the filtrate to 250 c.cs. and precipitate sulphide metals by passing sulphuretted hydrogen gas, filter off the sulphides, and test the filtrate; if precipitation is complete, boil off all traces of sulphuretted hydrogen and precipitate nickel as in PAR. 52, and estimate either gravimetrically (PAR. 21), or volumetrically, as in PAR. 95.

(f) *Bismuth*.—To 1-2 grams of the sample, according to the richness in bismuth, add 40 c.cs. nitric acid (1-2), and heat till the soluble portion has dissolved; add 5-10 c.cs. sulphuric acid and evaporate to 25 c.cs. bulk,

add 60 c.cs. water, boil, and allow to settle. Filter off lead sulphate, and wash thoroughly. To the filtrate, if blue due to the presence of copper, neutralize with ammonia and add potassium cyanide solution till colourless, and precipitate bismuth by passing sulphuretted hydrogen to saturation, filter off the black precipitate and wash thoroughly. Redissolve the precipitate by passing hot dilute nitric acid (1-3) through the filter, and wash thoroughly.

Dilute the solution to 250 c.cs. and proceed with the precipitation and estimation of bismuth as in PAR. 3.

(g) *Zinc*.—Zinc is sometimes found in the composition of the alloys, though not frequently, and may be estimated thus—

Digest 1-2 grams sample in nitric acid water (1-2) till the soluble portion has dissolved, filter off tin and antimony oxides, wash thoroughly, dilute to 250 c.cs., and through the filtrate pass sulphuretted hydrogen gas and filter off the sulphides, testing the filtrate as usual. From the filtrate boil off H_2S completely, evaporate to 100 c.cs. and precipitate any iron and alumina present by oxidation, first with 5 c.cs. of nitric acid and boiling, after which add ammonium chloride solution and ammonia in excess. Filter off any precipitate, and wash thoroughly.

To the filtrate add ammonium sulphide, which precipitates zinc. Boil, and allow to settle completely. Filter, taking the precautions recommended in PAR. 152 (f) (no need to wash), redissolve from the filter-paper by pouring hot dilute sulphuric acid (1-4) through, and estimate zinc by the ferrocyanide process (PAR. 82).

(h) Zinc, iron, aluminium, and other impurities found in very small quantities are best estimated under their various headings in the refraction of lead and tin (PARS. 146 and 148).

154. ZINC BASE ALLOYS.

These alloys usually consist of combinations of the following metals :—Zinc, copper, aluminium, tin, antimony, lead, and nickel. Lately calcium has been introduced in zinc lead alloys for the production of zinc base antifriction metals.

(a) *Zinc*.—Dissolve 1 gram of the sample by adding, carefully, dilute hydrochloric nitric acids (1-1-2), dilute to 250 c.cs., filter, and wash, and pass sulphuretted hydrogen gas through the filtrate, taking the precaution described in PAR. 148 (b). Filter into a 500 c.cs. flask, wash, and make up to 500 c.cs. with water. Pipette off 100 c.cs. of this solution = 2 gram sample, add excess of ammonia and ammonium sulphide to precipitate zinc, bring just to boiling point, and allow to settle. Filter, taking the precaution notified in PAR. 152 (f) (no need to wash), allow the filter-paper to drain thoroughly, dissolve the precipitate by pouring through the paper dilute hot sulphuric acid (1-4), and complete the estimation of zinc as described in PAR. 82.

(b) *Copper*.—Ignite the precipitate from sulphide metals (a) dissolve in nitric acid, using as little acid as possible, evaporate off all nitrous fumes, and filter off tin oxides, etc., and wash thoroughly with hot water. Evaporate to 40 c.cs. bulk, neutralize with ammonia, add 2 c.cs. ammonia in excess, and boil. Neutralize with acetic acid, add 5 c.cs. in excess, and boil. Allow to cool, and complete the estimation of copper by the hyposulphite method (PAR. 85).

(c) *Tin and Antimony*.—5 to 2 grams of the sample are taken, according to the richness of the alloy in tin, digested in nitric acid water (1-2), adding the acid carefully, and evaporated to about 10 c.cs. bulk. Take up again with 50 c.cs. water, boil, and allow to settle. If

antimony is present, conduct the separation as described in PAR. 45, and if absent, proceed with the estimation of tin gravimetrically, as described in PAR. 6, or volumetrically, as in PAR. 76.

(d) *Lead*.—As this is usually in small quantities or as an impurity, take 2 to 5 grams sample. Dissolve the sample taken in nitric acid water (1-2), boil, filter if necessary, and wash thoroughly. To the filtrate add 10 c.cs. sulphuric acid, boil, add methylated spirits carefully, as described in PAR. 1. If the precipitate obtained is very minute, filter, wash with methylated spirits water (1-6), ignite and sulphate as described in PAR. 1. If a large precipitate is obtained, take the precautions there directed, but it is advisable to use the volumetric method described in PAR. 79 for the completion of the estimation.

(e) *Aluminium*.—Aluminium is sometimes found in the composition of the alloy, but more often as an impurity. Digest 1 to 5 grams of the sample in nitric hydrochloric acid and water (1-1-3), till the soluble portion has dissolved, dilute to 250 c.cs. and pass sulphuretted hydrogen gas to completely precipitate all sulphide metals, filter off the precipitate, and wash thoroughly. From the filtrate boil off completely sulphuretted hydrogen gas, add 5 c.cs. nitric acid and boil to oxidize iron and alumina. Add 20 c.cs. ammonium chloride, excess of ammonia, boil and allow to settle. Filter off the precipitate, and preserve the filtrate for calcium. Treat the precipitate as described under separation of iron and alumina (PAR. 39).

(f) *Calcium*.—Calcium has been used lately in the composition of alloys of this class.

To the filtrate from iron and alumina (e) add excess of a solution of ammonium oxalate, boil, and allow to settle. Proceed with the estimation of calcium as in

PAR. 38, taking the precautions there directed, or treat volumetrically (PAR. 108).

(g) *Nickel*.—Nickel is found only occasionally in these alloys, and may be estimated thus—

Take .5 to 5 grams of the sample, according to the quantity of nickel present, and dissolve carefully in as little nitric acid water (1-2) as possible, evaporate to fastness, take up again with 5 c.cs. nitric acid and 50 c.cs. water, boil, and allow any precipitate to settle. Filter, and wash thoroughly. Neutralize carefully with ammonia, and add slight excess of a 5 per cent. solution of dimethylglyoxime, and proceed as in PAR. 21, gravimetrically, or PAR. 95, volumetrically. If the caustic soda method of precipitation is preferred, proceed as above till the point where tin and antimony oxides are filtered off, dilute to 250 c.cs. with cold water, and pass sulphuretted hydrogen gas to completely precipitate sulphide metals. Filter off the precipitate, and wash thoroughly. Boil off sulphuretted hydrogen gas, and evaporate to 100 c.cs. bulk. Precipitate iron and nickel by the addition of excess of caustic soda solution, filter, and wash. Redissolve from the filter-paper by pouring hot dilute nitric acid (1-4) through, and in the solution estimate nickel volumetrically as described in PAR. 95.

The various impurities present may be estimated as described under their various headings under refraction of metals.

155. ALUMINIUM ALLOYS.

Aluminium alloys usually consist of combinations of the following metals:—Aluminium, lead, copper, iron, nickel, magnesium, zinc, silicon, tin, antimony, and, since the advent of the aeroplane, tungsten, vanadium, molybdenum, and chromium have been used with more or less success.

(a) *Lead*.—Digest 2 grams of the sample in 50 c.cs. of a strong solution of caustic soda, on the hot plate, till the soluble portion has dissolved. The insoluble portion may consist of copper, lead, nickel, iron, and magnesium.

Filter off this precipitate, wash completely free from caustic soda, and preserve the filtrate. Ignite the precipitate in a porcelain capsule, dissolve it in nitric acid (1-3), and dilute to 200 c.cs. with cold water. Pass sulphuretted hydrogen gas till the copper and lead have completely precipitated out, filter off the precipitate, and preserve the filtrate. Dissolve the precipitate in as little nitric acid as possible, add 10 c.cs. sulphuric acid, cover the beaker with a watch-glass, and evaporate till dense white fumes are given off. Cool, dilute carefully to 50 c.cs. with water, and treat the precipitated lead sulphate gravimetrically as described in PAR. 1, or volumetrically as in PAR. 79.

(b) *Copper*.—To the filtrate from lead (a) add ammonia, carefully, till neutral, add 2 c.cs. in excess, and boil. Acidify with acetic acid, add 5 c.cs. in excess, boil, and allow to cool to the room temperature. Complete the estimation of copper by the hyposulphite method (PAR. 85).

(c) *Iron*.—Boil the filtrate from the sulphide metals till completely free from sulphuretted hydrogen, add 5 c.cs. nitric acid, and boil to 100 c.cs. bulk. Precipitate iron by means of ammonia and ammonium chloride. Estimate gravimetrically (PAR. 12), or volumetrically (PAR. 87 or 90), as desired.

(d) *Nickel*.—The dimethylglyoxime process may be used to precipitate nickel (PAR. 21), and the nickel redissolved and estimated volumetrically as in PAR. 95, or to the ammoniacal filtrate from iron add ammonium sulphide to precipitate nickel sulphide.* Filter, and

* Precaution—see PAR. 52.

wash, preserving the filtrate for magnesium. Dissolve the precipitate from the paper by passing hot dilute nitric acid (1-3) through it, wash thoroughly, boil for 10 minutes, and reprecipitate nickel by means of caustic soda. Estimate nickel gravimetrically as described in PAR. 20, taking the usual precautions there mentioned, or volumetrically as described in PAR. 95.

(e) *Magnesium*.—To the filtrate from the dimethylglyoxime add nitric acid and boil to completely destroy excess of that solution, or, if the ammonium sulphide method was used, add nitric acid and boil to completely oxidize any precipitated sulphur. When the solution has cleared, cool, add ammonia in excess and precipitate magnesium by the phosphate method as described in PAR. 32, or treat volumetrically (PAR. 94).

(f) *Zinc*.—Dilute the caustic soda filtrate from (a) to 250 c.cs., and pass sulphuretted hydrogen gas to completely precipitate zinc as zinc sulphide, with some aluminium sulphide, taking the precautions described in PAR. 152 (f). Filter off the precipitate (no need to wash), allow to drain thoroughly, redissolve the precipitate by passing hot dilute sulphuric acid (1-4) through it, wash thoroughly, and proceed with the estimation of zinc as described in PAR. 82.

(g) *Silicon*.—Dissolve 2 grams of the sample in 20 c.cs. nitric acid and 30 c.cs. water, evaporate to fastness, redissolve in 10 c.cs. nitric acid and 80 c.cs. of water, boil, and allow the precipitate, which consists of silicon, tin, and, if present, antimony, to settle. Filter through a fine Swedish filter-paper, wash thoroughly, and preserve the filtrate. Wash the precipitate from the paper into a beaker, add 20 c.cs. hydrochloric acid, and boil till the oxides of tin and antimony have completely dissolved. It will assist solution if, from time to time, a small crystal of potassium chlorate is added. Dilute the solution to

80 c.cs. and filter off the silica, wash thoroughly, ignite and weigh as SiO_2 . Factor = .46703 silicon.

(h) *Antimony*.—Antimony is sometimes found up to 2 per cent., and if found may be estimated thus—

Evaporate the filtrate from the solution of oxides of tin and antimony to small bulk, and precipitate antimony by adding freshly precipitated copper, as described in PAR. 45. Filter off the precipitated antimony and added copper, and preserve the filtrate for tin. Treat the precipitated copper and deposited antimony precipitate as described in PAR. 45.

(i) *Tin*.—Tin is estimated in the filtrate from antimony (h) by the sulphide method as described in PAR. 5.

(j) *Aluminium*.—Digest 2 gram of the sample in strong caustic soda solution till the soluble portion has dissolved. Filter off any precipitate, and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, add 20 c.cs. ammonium chloride, and precipitate alumina with slight excess of ammonia. As this precipitate is rather bulky for manipulation, a method whereby the precipitate is obtained in a granular form is to add a large excess of sodium hyposulphite to the acidified filtrate above, and boil till the sulphurous acid has been driven off. Alumina is thus precipitated in a dense powder, which is filtered, washed thoroughly, ignited, and weighed as alumina, Al_2O_3 .

An alternative method is the phosphate method described in PAR. 15.

(k) *Tungsten*.—Dissolve 2 grams of the sample in caustic soda solution, using as little in excess as possible, filter, and wash thoroughly. Heat to boiling and treat with a few c.cs. of a solution of 50 grams stannous chloride in 200 c.cs. hydrochloric acid. The amount should be regulated approximately to 20 c.cs. solution to every 15 gram tungsten trioxide present. After the solution

has boiled for some minutes, tungsten separates out in the form of a blue precipitate, W_2O_6 . Allow to settle, filter through a fine filter-paper, wash with a 5 per cent. hydrochloric acid solution. Ignite in a porcelain crucible, cool in a desiccator, and weigh as tungsten trioxide. The filtrate contains molybdenum.

Factor = .7931 tungsten.

(l) *Molybdenum*.—To the filtrate from tungsten add 5–10 grams zinc which has passed through a 20-mesh sieve, which precipitates tin in the metallic form. Filter and wash this precipitate thoroughly. The filtrate contains all the molybdenum present, neutralize the solution carefully, add a slight excess of lead acetate solution, which precipitates molybdenum, boil, and allow to settle. Filter, wash with hot water, dry, and separate from the paper. Ignite the paper completely, add the precipitate, and continue the ignition till constant in weight. Weigh as PbO , MoO_3 .

Factor = .26158 molybdenum.

(m) *Vanadium*.—Dissolve 2 grams of the sample in a mixture of 40 c.cs. water, 40 c.cs. sulphuric acid, and 2 c.cs. nitric acid, and boil. Filter off the residue, ignite and fuse with 1 part carbonate of soda and 2 parts of nitrate of potash. Extract the fusion with water, and filter. To the solution, which is yellow if chromium is present, add dilute nitric acid carefully, stirring all the time till only very slightly alkaline; filter off any precipitate, and add a solution of barium chloride and ammonia, which precipitates vanadium and chromium. Boil the precipitate with slight excess of sulphuric acid, and filter off sulphate of barium, wash, and to the reddish-yellow filtrate add ammonia, evaporate to small bulk, and add a piece of solid ammonium chloride, when vanadate of ammonium separates out. Filter off vanadium, wash thoroughly with hot water containing a little ammonium chloride,

and preserve the filtrate. Ignite and weigh the precipitate as vanadic oxide.

Factor = .5614 vanadium.

(n) *Chromium*.—Add sulphurous acid to the filtrate from ammonium vanadate (m), which will precipitate chromium as hydrated oxide. Filter, wash with hot water, ignite and weigh as Cr_2O_3 .

Factor = .686 chromium.

The impurities in the aluminium alloy may be estimated as described under their various headings in the refraction of metals.

CHAPTER XI

COAL, WATERS, FIRECLAY, ETC.

156. BOILER FEED WATERS.

It is customary to report the impurities present in terms of grains per gallon.

(a) *Total Solids*.—Evaporate 1 litre of the water under examination to dryness on a water bath, in a platinum capsule, adding a little at a time till the total quantity has been added. Continue heating till the residue is constant in weight.

Weigh as total solids.

(b) *Mineral Matter*.—Ignite the total solid of (a) till constant in weight, and weigh as mineral matter.

(c) *Organic Matter*.—Deduct the weight of mineral matter (b) from the weight of total solids (a) and report as organic matter.

(d) *Scale-forming Constituents*.—Treat the total mineral matter (b) with hot water, free from carbon dioxide, 10 c.cs. at a time, five times, filtering each 10 c.cs. through a fine filter-paper, ignite the filter-paper in the platinum capsule, deduct the weight of ash, and weigh as scale-forming constituents.

(e) *Non-scale forming Constituents*.—Deduct the weight obtained from the total mineral matter (b) to find the non-scale forming constituents.

Silica, iron oxide, alumina, calcium, magnesium constituents are estimated as follows:—

(f) *Silica*.—To the residue (d) add 10 c.cs. hydrochloric acid, and evaporate to dryness. Take up with 10 c.cs.

hydrochloric and 40 c.cs. distilled water, boil, filter off silica, ignite, and weigh as silica.

(g) *Iron and Alumina*.—Add 5 c.cs. nitric acid, and boil to oxidize iron and alumina, precipitate the oxides by adding excess of ammonia, and proceed with the separation as described in PAR. 39.

(h) *Lime*.—Estimate in the filtrate (g) as described in PAR. 38.

(i) *Magnesia*.—Estimate in the filtrate (h) as described in PAR. 32.

(j) *Sulphuric Acid*.—Evaporate the filtrate from (i) to 100 c.cs. bulk, add 10 c.cs. hydrochloric acid, and boil. Precipitate sulphuric acid by means of barium chloride, and proceed as described in PAR. 30. Calculate the BaSO_4 found to SO_3 .

(k) **CALCULATION OF SCALE-FORMING CONSTITUENTS**.—Calculate the SO_3 to CaSO_4 . The remaining CaO and the MgO are calculated to carbonates.

The iron to Fe_2O_3 , alumina Al_2O_3 and the insoluble siliceous matter is reported as weighed. The sum of the above should be equal to the weight of the scale-forming constituents. For a complete report the filtrate from the scale-forming constituents should also be examined for iron, alumina, lime, and magnesia.

(l) *Chlorine*.—To 100 c.cs. of the water under examination add a crystal of potassium chromate, and titrate with N/10 silver nitrate till a faint red-brown permanent precipitate is formed. The N/10 silver nitrate is made by dissolving 3.4 grams silver nitrate in 200 c.cs. of distilled water. 1 c.c. = approximately .00355 gram chlorine, but should be tested against a solution of salt, thus:—Weigh out accurately 5.85 grams pure sodium chloride and dissolve in 1 litre of water. Pipette off 20 c.cs. and titrate as above. 20 c.cs. of the salt solution should require exactly 20 c.cs. of N/10 silver nitrate.

(m) **TOTAL SULPHURIC ACID.**—To 100 c.cs. of the water under examination add 10 c.cs. hydrochloric acid and slight excess of barium chloride solution, and boil; complete the examination as described in PAR. 30, and calculate to SO_3 .

(n) **Temporary Hardness.**—Colour 200 c.cs. of the sample with 5 drops methyl orange and titrate with N/1 sulphuric acid till a permanent pink colour is produced. Calculate to temporary hardness by multiplying the c.cs. consumed by .05.

(o) **Total Hardness.**—Calculate lime and magnesia to carbonate of lime and bring to grains per gallon.

Subtract the temporary hardness (n), and report the remainder as permanent hardness.

(p) **Softening Water.**—Water is usually softened by adding lime and sodium carbonate. The lime precipitates calcium from solution as carbonate and the magnesium as hydrate. The sodium carbonate also precipitates calcium as carbonate.

To determine how much of the reagents to use, boil an accurately measured sample of the water with an accurately measured volume of $\text{Ca}(\text{OH})_2$, the added excess being accurately titrated by means of N/1 sulphuric acid, using methyl orange as an indicator. Then add to the titrated solution excess of standard sodium carbonate solution, boil, cool, allow to settle, and filter. Titrate excess of Na_2CO_3 in the filtrate. From the i obtained above, the quantity per gallon of wate. easily be deduced.

157. FIRECLAYS AND FIREBRICKS.

(a) **Moisture.**—Dry 10 grams in the water bath till constant in weight. The loss is moisture.

(b) **Organic Matter.**—Ignite the dry sample from (a)

till constant in weight, and report the additional loss as organic matter.

(c) *Silica*.—Grind 2 grams of the sample very fine in an agate mortar, and ignite till constant in weight, mix with 20 grams of fusion mixture consisting of equal parts of sodium and potassium carbonates, fuse for 20 minutes, and cool. Dissolve the fusion in dilute hydrochloric acid in a porcelain basin, evaporate to dryness, take up with 20 c.cs. hydrochloric acid and 100 c.cs. water, boil, allow to settle, and filter. Wash thoroughly, ignite and weigh. Hydrofluorize, as described in PAR. 24, twice, and when ignited till constant in weight, deduct from the first weight obtained. The loss is silica. Dissolve the residue in hydrochloric acid and add to the filtrate.

(d) *Iron and Alumina*.—To the filtrate (c) add ammonium chloride and excess of ammonia, boil, and allow the precipitated oxides of iron and alumina to settle. Filter, wash thoroughly, and conduct the separation of iron and alumina as described in PAR. 39.

(e) *Lime*.—Evaporate the filtrate from (d) to 150 c.cs. bulk, and precipitate lime by means of a solution of ammonium oxalate, and proceed with the estimation of lime as in PAR. 38.

(f) *Magnesia*.—Estimate magnesia in the filtrate from (e), as described in PAR. 32.

(g) *Alkaline Salts*.—Weigh out, in a platinum capsule, 2 grams of the very finely ground sample and add gradually hydrofluoric acid, and heat very gently for some time, add sulphuric acid very cautiously, and hydrofluorize the silica. Repeat this operation till the silica is completely hydrofluorized, while the bases are converted into sulphates. Cool, add hydrochloric acid to dissolve the sulphates, evaporate off the excess of acid, dilute, and transfer to a beaker. Heat and add baryta water Ba(OH)_2 till no further precipitate is obtained. By this means the

sulphuric acid, alumina, iron, and magnesia are all precipitated, filter, and wash thoroughly. Evaporate the filtrate to 100 c.cs. bulk, remove barium and traces of lime by means of ammonium carbonate, filter, wash the precipitate and evaporate the filtrate to very small bulk, transfer to a platinum capsule, evaporate to dryness, and ignite, to drive off ammonium salts. Dissolve in a little water, add more ammonium carbonate, to ensure the complete removal of barium and calcium, filter into a weighed platinum capsule, add a few drops of hydrochloric acid and evaporate to dryness. Ignite, and weigh the remaining alkali as chlorides.

Estimate the potash thus—

(h) *Potash*.—To the alkalies obtained in (g) add water, a few drops of hydrochloric acid, and heat till dissolved, add a slight excess of platinum chloride solution (7 grams per 100 c.cs.) and evaporate to dryness on a water bath, and allow to stand for half an hour, add a few more drops of platinum chloride, take up with methylated spirits, and decant through a fine Swedish filter-paper. Wash the precipitate by decantation, and wash the paper also with methylated spirits, till the washings are quite colourless. Transfer the precipitate to the paper and wash three times. Dry the precipitate in the water bath, and separate the precipitate as carefully as possible, and ignite the filter-paper in the capsule. Transfer the precipitate to the capsule, dry in the water bath till constant in weight, and weigh as K_2PtCl_6 . To find the K_2O therein multiply by 193.

Calculation of Alkaline Salts.—Calculate the K_2O (h) to KCl and subtract the result from the total alkaline salts (g). Calculate the remaining $NaCl$ to Na_2O .

Fireclay and firebrick analyses are conducted exactly alike.

158. COAL PROXIMATE ANALYSIS.

(a) *Sampling*.—In taking samples of coals and cokes a large number of pieces should be broken off the lumps, a proportionate quantity should be taken from the rubble, and a proportionate quantity from the fine, thus: the sampler estimates the quantity of lumps to be 72 per cent., rubble 16 per cent., and small 12 per cent. The sample sent to the sample room should consist of these proportions also. This sample is broken down to the size of beans, thoroughly mixed and quartered. One quarter is taken and further pulverized to the size of small peas, and a sample of about 1 lb. taken, the remainder quartered, and two opposite quarters taken. This sample is now subjected to a further pulverization, and an average sample taken. This average sample is powdered to pass through a 10-mesh sieve and about 1 lb. bottled and sent to the laboratory along with the first reserved portion.

(b) *Moisture*.—Weigh out 5 grams of the sample and dry in the water bath till constant in weight. The loss is moisture.

(c) *Specific Gravity*.—Place 50 c.cs. of distilled water in a graduated 100 c.cs. measure, add 30 grams of the sample, taken from the first reserve portion the size of peas. Tap the measure to get rid of all air bubbles, note the number of c.cs. displaced, and divide by 30 to arrive at the specific gravity.

(d) *Volatile Matter*.—Heat 2 grams of the sample, in a deep platinum crucible, fitted with a lid, over a bunsen flame for $3\frac{1}{2}$ minutes, and for 1 minute over the flame from a foot blowpipe. The loss in weight is volatile matter and the residue is coke.

(e) *Mineral Matter*.—Heat 5 grams of the sample in a muffle furnace till the carbon has completely burned off,

and weigh the remaining ash. It is customary also to report the colour of the mineral matter.

(f) *Sulphur*.—Mix 2 grams of the sample with 5 grams of slaked lime, in which the sulphur has been estimated, and heat in a muffle furnace till the mixture becomes white throughout. Transfer to a beaker, and boil up with hydrochloric acid water (1-2), dilute to 100 c.cs. with boiling water, allow to settle and filter. Precipitate the sulphur, by means of a solution of barium chloride in slight excess, boil, allow to settle, filter through a fine filter-paper, wash thoroughly, ignite, and weigh. Subtract the sulphur content of 5 grams of slaked lime, and calculate to percentage.

(g) *Phosphorus*.—Ignite 10 grams of the sample in a muffle, transfer the ash to a beaker, boil with hydrochloric acid, and evaporate to dryness on the hot plate. Cool, take up with 10 c.cs. hydrochloric acid, 50 c.cs. of water, and boil. Filter, add excess of ammonia, evaporate to 50 c.cs. bulk, acidify slightly with nitric acid, and complete the estimation of phosphorus as described in PAR. 28 or PAR. 29.

The volatile matter consists of sulphur moisture, gas, tar, etc., and the coke of fixed carbon, sulphur, and ash. As the sulphur distributes itself in definite proportions, it is easy to calculate how much is contained in each. The sulphur always varies directly as the coke.

Example.—Suppose the coal contains 1·82 per cent. sulphur, 56·94 per cent. coke, 43·06 per cent. volatile matter, therefore $100 : 56·94 : 1·82$. Sulphur in coke 1·03 per cent., and sulphur in volatile matter 79 per cent. To find gas, tar, etc., add the moisture to the sulphur in volatile matter and subtract from the volatile matter, the remainder is classed as gas, tar, etc.

To calculate the fixed carbon, add the ash and sulphur in coke and subtract from the coke. The remainder is fixed carbon.

(h) *Practical Heating Power—Playfair's Formulae.*—Multiply the fixed carbon in 1 part by 13, and the volatile matter in 1 part by 3.1, and add both results together. The answer is lbs of water at 212° F. which can be converted into steam by 1 lb. of coal.

The weight of 1 cubic foot is obtained by multiplying the specific gravity by 62.5

159. ULTIMATE COAL ANALYSIS.

(a) and (b) *Carbon and Hydrogen.*—Weigh out 3 grams of the dry powdered sample in a platinum boat and insert

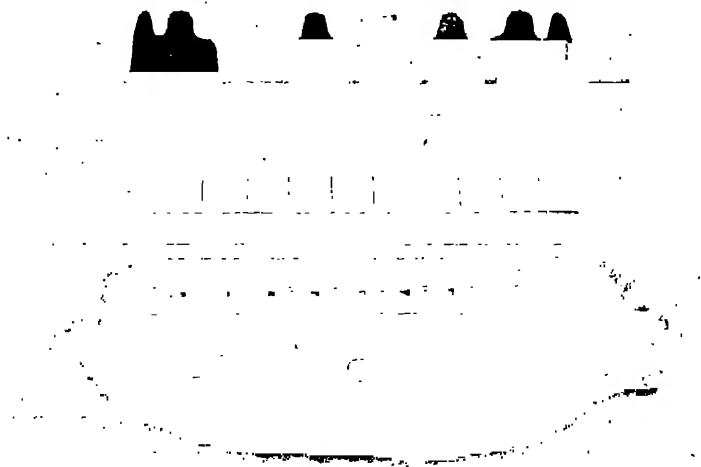


FIG. 29.—Combustion Furnace.

into the combustion tube. At either end of the tube place some ignited copper oxide and a loose-fitting wad of freshly ignited asbestos. Pass a current of pure dry oxygen through the apparatus, and make the attachment of the collecting apparatus. This consists of a weighed calcium chloride tube, to collect the hydrogen, which is evolved in the form of water, and potash bulbs containing 50° Twaddell caustic soda, to collect the carbon generated,

as carbon dioxide. Continue to pass the stream of oxygen, and raise the temperature gradually. When the reaction is complete, weigh the tubes and calculate to per cent. ; $\frac{1}{2}$ of the increase in weight of the calcium chloride tube is hydrogen, and $\frac{3}{11}$ of the increase in weight of the potash bulbs is carbon.

(c) *Oxygen*.—Is usually done by difference.

(d) *Nitrogen*.—Mix 2 grams of the sample with 20 grams soda lime, and insert into a combustion tube with one end closed, and insert a loose wad of freshly ignited

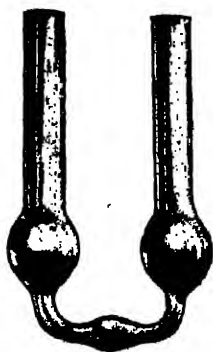


FIG. 30.—Calcium Chloride Tube.



FIG. 31.—Potash Bulb.

asbestos. Attach to this tube, by means of a perforated cork, a set of nitrogen bulbs, Fig. 32, containing 10 c.cs. of $N/1$ sulphuric acid. Now tap the tube lengthwise in order to leave a clear space above the soda lime and sample, leaving about 6 inches of clear space towards the mouth of the tube. Place the tube in the gas furnace, leaving 3 inches protruding, and commence heating at the cork end. The heating should be carried back gradually so that the bubbles come off separately, and the tube should only be heated to a dull red heat. Turn off the gas when the bubbles cease to pass through the bulbs, allow to cool, and again heat to expel the air which has been inhaled.

Detach the bulbs, transfer the liquid to a porcelain basin, and titrate the N/1 acid, by means of N/1 soda, using litmus as an indicator. Subtract the number of c.cs. consumed from 10 c.cs. (original N/1 sulphuric acid), and multiply the remainder by .014 to find the nitrogen in the sample used.

(e) *Sulphur*.—Estimate sulphur as in (f), proximate analysis.

(f) *Mineral Matter*.—Estimate mineral matter as in (e), proximate analysis.

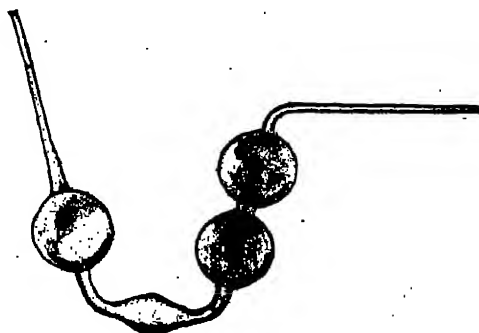


FIG. 32.—Nitrogen Bulbs.

(g) *Phosphorus*.—Estimate in the mineral matter as in (g), proximate analysis.

(h) *Moisture*.—Estimate moisture as in (b), proximate analysis.

As carbon, hydrogen, and nitrogen are estimated in the dried sample, calculate to the original sample by subtracting the moisture from 100 and multiplying the carbon, hydrogen, and nitrogen by the figure obtained, and dividing by 100.

Theoretical Heating Power.—(1) Calculate the oxygen to H_2 and subtract the latter from the total hydrogen in 1 part of coal.

(2) Multiply the hydrogen left by 61920.

- (3) Multiply the carbon in 1 part by 14544.
- (4) Add together answers of (2) and (3)=Heat units, Fah.

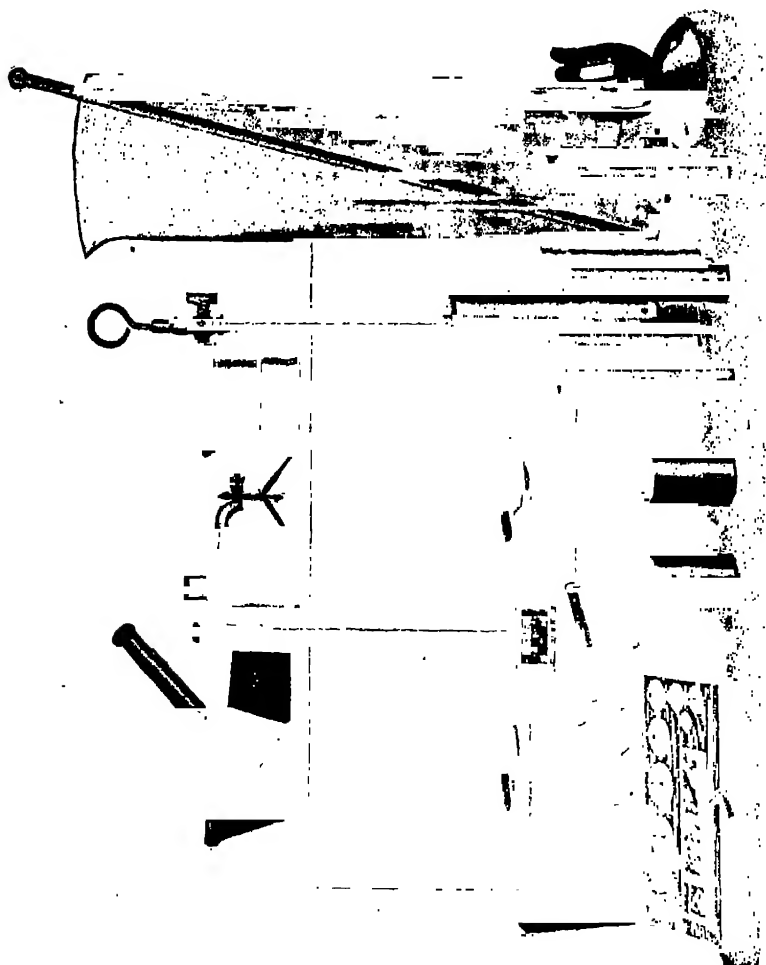


FIG. 33.

- (5) Divide the result at (4) by 972, and the result is the theoretical heating power in lbs. of water at 212° F. converted into steam by 1 lb. of coal.

NOTE.—During combustion, calcium and magnesium carbonates, when present in coal, evolve carbon dioxide which is absorbed in the potash bulbs, causing the result for carbon to be too high. When oxygen is estimated by difference, an error is introduced if the ash of the coal is not treated with ammonium carbonate and again ignited before weighing. Unless the necessary corrections are made the true value of the calorific power cannot be calculated from the results of the analysis.

ESTIMATION OF CALORIFIC POWER.

The calorific power of fuel is determined by ascertaining the number of heat units which are evolved by the combustion of unit weight of the fuel in oxygen.

One heat unit of "calorie" is the amount of heat which is required to raise the temperature of one gram of water one degree Centigrade. Fig. 33 is an illustration of a Lewis Thomson calorimeter, one of the many excellent calorimeters on the market at the present time.

A very complete description of this apparatus and method of manipulation is supplied with each instrument.

CHAPTER XII

USEFUL DATA

FACTORS FOR GRAVIMETRIC ANALYSIS

Required.	Weighed as.	Factor.
Ag	AgCl	.7526
Al	Al ₂ O ₃	.53033
"	AlH ₂ O ₄	.22187
As	As ₂ O ₃	.6092
As	Mg ₃ As ₂ O ₇	.48275
Bi	Bi ₂ O ₃	.89677
"	BiO ₃ (Cr ₂ O ₃) ₃	.62561
Ca	CaO	.71429
"	CaCO ₃	.4000
Co	Co ₂ O ₄	.73444
"	Co ₃ P ₂ O ₄	.4040
Cr	Cr ₂ O ₃	.6842
Cu	CuO	.7989
Fe	Fe ₂ O ₃	.7000
Mg	Mg ₃ P ₂ O ₇	.21875
Mn	Mn ₂ O ₄	.70252
Ni	C ₄ H ₁₁ O ₁₁ N ₄ Ni	.2032
Ni	NiO	.7858
Pb	PbOCrO ₃	.63993
Pb	PbSO ₄	.68293
P	Phospho Molybdate	.0163
"	Mg ₃ P ₄ O ₇	.2787
Sb	Sb ₂ O ₄	.78948
"	Sb ₂ S ₃	.7130
Si	SiO ₂	.46703
Sn	SnO ₂	.78738
S	K ₂ SO ₄	.13732
Ti	TiO ₂	.6098
W	WO ₃	.7931
Ur ₂ O ₅	Ur ₂ O ₅	.8760
V	V ₂ O ₅	.5604
Zn	ZnO	.80344
ZnS	ZnS	.67104
Zn	Zn ₃ P ₂ O ₇	.4289

COLORIMETRIC STANDARDS.

Substance.	Grams per litre.	Estimation.	Factor.
Iron Alum	8.606	Iron	.001
Stannous Chloride	1.300	Tin	.001
Copper Sulphate	3.930	Copper	.001
Ammonium Vanadate	1.000	Vanadium	dilute to .0001
Potassium Permanganate287	Manganese	.0001
Potassium Titanic-Fluoride600	Titanium	.002
Titanium Oxide	1.000	Titanium	dilute to .002
Nickel Sulphate	4.790	Nickel	.001
Ferric Chloride	{ known strength diluted }	Iron	dilute to .001
Zinc Sulphate	4.396	Zinc	.001
Lead Acetate	1.831	Lead	.0001
Potassium Bichromate	2.827	Chromium	.001
Ammonium Molybdate	10.208	Molybdenum	.005
Bismuth100	Bismuth	.0001
Cobalt Nitrate	5.983	Cobalt	.001
Tungstic Acid	1.261	Tungsten	.001

STANDARD SOLUTIONS FOR VOLUMETRIC ESTIMATIONS.

Substance.	Grams per litre.	Estimation.	Approximate Factor.
N/10 Iodine	12.80	Tin	.0060
Methylene Blue	4.00	Tin	.002
N/10 Sodium Hyposulphite	25.00	Antimony	.0061
" " " "	"	Copper	.00635
" " " "	"	Lead	.01035
" " " "	"	Cobalt	.0058
" " " "	"	Iron	.0056
Potassium Ferricyanide	14.06	Zinc	.0041
Potassium Ferrocyanide	21.63	Zinc	.0062
Sodium Sulphite	7.00	Lead	.0150
Sodium Sulphide	{ NaOH 1.05 Sp. Gr. saturated with H ₂ S }	Zinc	.005
N/10 Ammonium Molybdate	9.00	Lead	.01
N/10 Potassium Bichromate	4.92	Iron	.0056
" " " "	"	Chromium	.0052
" " " "	"	Manganese	.00275
N/10 Sulphuric Acid	49.043	Phosphorus	.00044
N/10 Caustic Potash	56.00	Magnesium	.0017
Uranium Acetate	29.00		

USEFUL DATA

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Substances.	Grams per Litre.	Estimation.	Approximate Factor.
Arsenious Acid	1'00	Manganese	'005
Stannous Chloride	15'45	Ferric Iron	'05
Potassium Cyanide	50'00	Copper	'007
Iodine	1'69	Arsenic	'0005
Silver Nitrate and Potassium {	1'00	Nickel	'0025.]]
Cyanide	12'00		
Sodium Phosphate	29'835	Uranium	'02
N/10 Potassium Permanganate	3'160	Bismuth	'0104
" " "	"	Cadmium	'0086
" " "	"	Calcium	'0020
" " "	"	Oxalic Acid	'0045
" " "	"	Ferrous Sulphate	'0278
" " "	"	Ferrous Ammonium Sulphate	'0392
" " "	"	Uranium	'01191
" " "	"	Titanium	'00481
" " "	"	Vanadium	'0051
Ammonium Sulphocyanide	7'80	Silver	'61
Lead Acetate " "	"	Arsenic	'0025
Sulphuric Acid 1'84 Sp. Gr.	19'50	Molybdenum	'005
Caustic Potash	8'3 cc.	Aluminium	'00265
Barium Chloride	16'4		
	36'25	Sulphur	'005

METAL STANDARDS.

Metal.	Symbol.	Atomic Weight.	Sp. Gr.	Sp. Heat.	M. P. Cent.	Elect. Conduct. Ag 100.	Coeff. of Linear Expansion.
Aluminium	Al	27'1	2'36	'218	657	57'3	'0000231
Antimony	Sb	120'2	6'71	'051	630	4'6	'0000105
Arsenic ..	As	75	5'67	'081	450	4'7	'0000055
Barium ..	Ba	137'4	3'78	'047	850	1'3	'0000162
Bismuth ..	Bi	208	9'80	'031	266	1'3	
Cadmium	Cd	112'4	8'60	'056	322	14'7	'0000306
Cesium ..	Cs	132'8	1'87	'048	26	3'7	
Calcium ..	Ca	40'1	1'57	'170	780	22'1	
Cerium ..	Ce	140'2	6'68	'045	623		
Chromium	Cr	52	6'80	'120	1482		
Cobalt ..	Co	59	8'50	'103	1464	15'6	'0000123
Columbium	Cb	93'5	12'70	'071			'0000167
Copper ..	Cu	63'6	8'93	'093	1084	94'0	
Gallium ..	Ga	69'9	5'90	'079	30		
Glucinum..	Gl	9'1	1'93	'631			

METAL STANDARDS—*Continued.*

Metal.	Symbol.	Atomic Weight.	Sp. Gr.	Sp. Heat.	M.P. Cent.	Elect. Conduct. Ag 100.	Co-eff. of Linear Expansion.
Gold ..	Au	197.2	19.32	.031	1065	66.8	.0000144
Indium ..	In	114.8	7.42	.057	155	16.5	.0000417
Iridium ..	Ir	193.1	22.42	.033	1950		.0000070
Iron ..	Fe	55.8	7.86	.110	1505	16.2	.0000121
Lanthanum	La	139	6.20	.045	810		
Lead ..	Pb	207.1	11.37	.031	327	7.2	.0000292
Lithium ..	Li	69	.54	.941	186	17.5	
Magnesium	Mg	24.3	1.74	.250	633	33.7	.0000269
Manganese	Mn	54.9	8.00	.120	1207		
Mercury ..	Hg	200.6	13.59	.032	—39	1.6	.0000610
Molybdenum	Mo	96	8.60	.072	2500		
Nickel ..	Ni	58.7	8.88	.108	1427	21.2	.0000127
Osmium ..	Os	190.9	22.48	.031	2500	15.5	.0000065
Palladium	Pd	106.7	11.50	.059	1535	14.5	.0000117
Platinum ..	Pt	195.2	21.58	.032	1710	13.4	.0000089
Potassium	K	39.1	.86	.170	62	20.8	.0000841
Rhodium ..	Rh	102.9	12.10	.058	1660		.0000085
Rubidium ..	Rb	85.5	1.53	.077	38		
Ruthenium	Ru	101.7	12.26	.061	1800		.0000096
Silver ..	Ag	107.9	10.53	.056	961	100	.0000192
Sodium ..	Na	23.0	.97	.290	95	37.3	.0000710
Strontium	Sr	87.6	2.54		800	6.7	
Tantalum	Ta	181.5	10.80	.036	2910	9.8	.0000079
Tellurium	Te	127.5	6.25	.049	440	6.8	.0000167
Thallium ..	Tl	204	11.85	.033	303	8.3	.0000302
Thorium	Th	232.4	11.10	.028			
Tin ..	Sn	119	7.29	.055	232	11.3	.0000223
Titanium	Ti	48.1	4.87	.130			
Tungsten	W	184	19.10	.034	3100	1.7	
Uranium ..	U	238.5	18.70	.028			
Vanadium	V	51	5.50	.125	1680		
Yttrium ..	Yt	89	3.80				
Zinc ..	Zn	65.4	7.15	.094	419	25.2	.0000291
Zirconium	Zr	90.6	4.15	.066	1500		

USEFUL DATA.

RELATION OF DEGREES TWADDELL TO SPECIFIC GRAVITY.

The relation of Degrees Twaddell to the specific gravity of a liquid is most readily stated by assuming the specific gravity of water to be 1000 instead of unity. On this assumption

$$\text{Degrees Twaddell} = \frac{\text{Sp. Gr.} - 1000}{5}$$

$$\text{Specific gravity} = \text{Degrees Twaddell} \times 5 + 1000$$

THERMOMETRIC SCALES.

Two different thermometric scales are in general use, Centigrade and Fahrenheit, the former being more generally used for scientific purposes. F° represents Fahrenheit, and C° a temperature in the Centigrade Scale; the two scales are mutually convertible by the following formulæ:—

$$F^{\circ} = \frac{9}{5} C^{\circ} + 32 \qquad C^{\circ} = \frac{5}{9} (F^{\circ} - 32)$$

CONVERSION TABLES.

WEIGHTS.					
<i>To Convert</i>					<i>Multiply by</i>
Grains to Grams	650
Ounces to Grams	28.35
Pounds to Grams	453.6
Pounds to Kilograms45
Cwts. to Kilograms	50.8
Tons to Kilograms	1016.0
Grams to Grains	15.43
Grams to Ounces353
Kilograms to Ounces	35.3
Kilograms to Pounds	2.2
Kilograms to Cwts.2
Kilograms to Tons001

MEASURES.

<i>To Convert</i>					<i>Multiply by</i>
Inches to Millimetres	25'4
Inches to Centimetres	2'54
Feet to Metres	'3048
Yards to Metres	'9144
Yards to Kilometres	'0004
Miles to Kilometres	1'6
Millimetres to Inches	'04
Centimetres to Inches	'4
Metres to Feet	3'3
Metres to Yards	1'1
Kilometres to Yards	1093'6
Kilometres to Miles	'62

CONVERSION TABLES.

1 Yard	'9144 Metre.
1 Sq. Metre	1'196 Sq. Yards.
1 Litre	1'760 Pints.
1 Litre	'22 Gallon.

To find the circumference of a circle

Multiply the diameter by 3'1416.

To convert cube into cylinder

Multiply by '7845

To convert cube into sphere

Multiply by '5236

1 cubic foot of air, at 0° C. and 760 mm. pressure, weighs 564'9 grams or '0807 lb.

To find the capacity of a tank or vessel in gallons, multiply the length, width and depth together in feet. This gives the capacity in cubic feet. Multiply the figure obtained by 6'24, to find the capacity in gallons. If the dimensions are in inches use the factor '003607 in place of 6'24 to find the number of gallons.

GENERAL DATA REGARDING WATER.

1 gallon multiplied by 277'46 = cubic inches.

Cubic inches multiplied by '003604 = gallons.

Cubic feet multiplied by 62'28 = lbs.

Pounds of water multiplied by '0166 = cubic feet.

Gallons of water multiplied by '004464 = tons.

Tons multiplied by 224 = gallons.

Cubic feet multiplied by '0278 = tons.

Tons multiplied by 35'97 = cubic feet.

A USEFUL SOLUTION FOR TESTING METALS IS AS FOLLOWS.

Nitric Acid	6 oz.
Potassium Bichromate	1 oz.
Water	2 oz.

One drop on the end of a glass rod is applied.

Metal.	Colour (1 minute).	Mark left.
Gold over 9 carat	Unchanged	No stain
Silver, Pure	Bright blood red	Grey white
„ 925	Dark red	D. brown
„ 800	Chocolate	D. brown
„ 500	Green	D. brown
„ German	Dark blue	Light grey
Nickel	Turquoise	Scarcely any
Copper	Very dark blue	Cleaned copper
Brass	Dark brown	Light brown
Lead	Nut brown	Leadon
Tin	Red brown	Steel
Zinc	Light chocolate	None
Aluminium	Yellow	None
Platinum	Vandyke	No stain
Iron	Various	Black

PLATINUM RESIDUES.

To the solution and residues, which usually contain sufficient methylated spirits, add sodium peroxide carefully and digest till the platinum is precipitated. Wash with hot water and finally with hot hydrochloric acid. Ignite and weigh. Dissolve the weighed quantity in aqua regia (hydrochloric 4, nitric 1), evaporate to dryness on the water bath, add hydrochloric acid, and again evaporate to dryness. Take up with dilute hydrochloric to the requisite

strength, a convenient dilution being 7 grams platinum chloride per 100 c.cs.

AMMONIUM MOLYBDATE RESIDUES.

Evaporate the acid residues to fastness, add a little cold water, filter, and wash with cold water. Dissolve the precipitate in ammonia, and add a slight excess of magnesia mixture. Filter off any phosphate, and evaporate till ammonium molybdate crystallizes out, keeping ammonia present in excess. Should a blue solution be obtained, due to lower oxides, add hydrogen peroxide.

TYPICAL ANALYSES.

COPPERS.

	Electrolytic.	Ingot.	Commercial Bar.
Copper	99'9850	99'440	99'146
Lead	'0016	'195	'308
Arsenic	'0010	'060	'054
Antimony	'0002	'005	'069
Bismuth	'0007	'009	—
Iron	—	'039	'133
Nickel	—	'073	'071
Sulphur	—	—	'185
	99'9885	99'821	99'966

TINS.

	Billiton.	Mt. Bischoff.
Tin	99'766	99'627
Antimony	'064	'133
Lead	'020	'080
Iron	'140	'120
Copper	—	—
Arsenic	—	—
Sulphur	—	Trace
	99'990	99'960

ANTIMONIES.

	Crude.	Star.
Antimony	94'444	99'588
Sulphur	1'951	161
Iron	2'753	189
Lead	221	Trace
Arsenic	539	Nil
	99'980	99'938

LEADS.

	Special Broken Hill.	Pure Commercial.	Hard Lead.
Lead	99'985	98'498	95'703
Cadmium	Trace	—	—
Silver	001	063	—
Antimony	011	348	3'546
Iron	002	034	280
Tin	—	968	223
Copper	—	072	220
Arsenic	—	—	—
	9'999	99'983	99'972

ALUMINIUMS.

American.

	1st Grade.	3rd Grade.
Aluminium	99'014	96'560
Tin	064	236
Lead	—	1'477
Iron	614	987
Magnesium	Trace	153
Copper	048	394
Silicon	164	186
	99'904	99'993

NICKELS.

	Special.	New Caledonian.
Nickel	99'201	98'230
Iron	'363	'977
Carbon	'165	'497
Silicon	'103	'303
Cobalt	'081	—
Copper	—	—
Manganese	'050	—
	99'963	100'007

BRASSES.

	Yellow Brass.	Muntz.	Delta.
Copper	70'230	59'905	56'523
Tin	'161	—	—
Lead	'283	'341	'136
Zinc	29'112	39'602	40'962
Iron	'135	'140	1'363
Manganese	—	—	'532
Aluminium	—	—	'461
	99'921	99'988	99'977

GUNMETAL AND BRONZE.

	Axis Bearings.	Gunmetal.
Copper	85'552	87'963
Tin	9'851	10'016
Zinc	3'773	1'967
Lead	'682	—
Iron	'084	'035
Phosphorus	'053	—
	99'995	99'981

USEFUL DATA

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NICKEL ALLOYS.

			German Silver.		Nickel Bronze.	Silveroid.
			Sheet.	Castings.		
Copper	57'196	48'673	77'909	45'113
Nickel	25'567	23'787	9'963	17'863
Zinc	22'643	24'162	—	35'423
Iron	255	434	987	120
Lead	162	2'771	1'018	1'368
Silicon	133	148	096	042
Tin	—	—	10'014	034
			99'956	99'975	99'987	99'963

BEARING METALS.

	Nickel Hardened.	Plastic.	Motor Bearings.	Mine Shaft Bearings.	Ship's Tunnel Bearing.
Tin ..	89'924	79'634	52'613	16'213	5'032
Lead ..	—	1'864	36'204	71'292	80'406
Antimony	6'003	11'567	9'872	11'961	14'452
Copper ..	3'106	6'823	1'297	498	—
Nickel ..	963	—	—	—	—
Iron ..	—	Trace	Trace	Trace	048
		99'996	99'888	99'986	99'964
					99'932

ZINC BASE ALLOYS.

	Anti-Friction.	Anti-Friction.	Stop Cook.	Zinc Aluminium Solder.
Zinc ..	68'962	51'750	71'039	79'345
Tin ..	19'036	45'764	20'937	131
Copper ..	4'103	1'602	6'875	7'943
Antimony	2'866	403	—	—
Lead	4'996	343	682	163
Iron ..	028	126	364	393
Aluminium	—	—	—	—
		99'991	99'988	99'897
				99'991

M

ALUMINIUM ALLOYS.

	Duralumin.	Wire.	
Aluminium	94'618	93'740	
Copper	3'913	'213	
Iron	'452	'373	
Magnesium	'754	1'586	
Silicon	'218	'192	
Tin	—	3'156	
Lead	—	'728	
	99'955	99'988	

FIRECLAYS.

	Glenboig.	Dowlis.	Australian.
Silica	56'42	67'12	73'391
Alumina	26'40	21'18	18'353
Iron Oxide	1'33	1'85	1'280
Lime (CaO)	'60	'32	'049
Magnesia (MgO)	—	'82	—
Alkalies	—	2'02	'018
Water and Organic Matter	13'75	7'21	5'120

FIREBRICKS.

	Stourbridge.	Wortley Leads.	Australian.
Silica	69'00	72'65	78'560
Alumina	27'30	23'75	19'316
Iron Oxide	1'86	1'75	1'336
Lime (CaO)	'27	'30	'426
Magnesia (MgO)	'32	'36	—
Potash K_2O	'65	'81	'162
Soda Na_2O	'26	'29	'089
	99'66	99'91	99'889

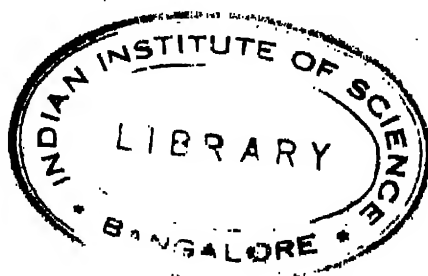
COAL.

PROXIMATE ANALYSIS.

Coke	50.70	
Volatile matter	49.30	
	<u>100.00.</u>	
Volatile matter { Gas, tar, etc.	37.908	49.300
{ Sulphur	.512	
{ Moisture	12.280	
Coke { Fixed carbon	45.552	50.700
{ Ash *	3.200	
{ Sulphur	.498	

* Contains phosphorus098 per cent.
Specific gravity	1.25
Weight of 1 cubic foot	78.125 lbs.
Heating power (practical)	6.44

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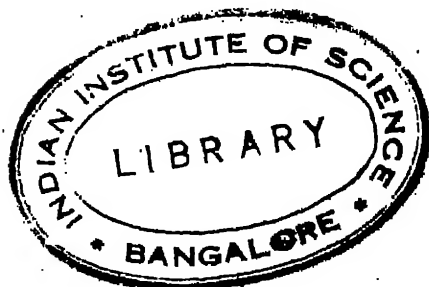
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C. S.



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